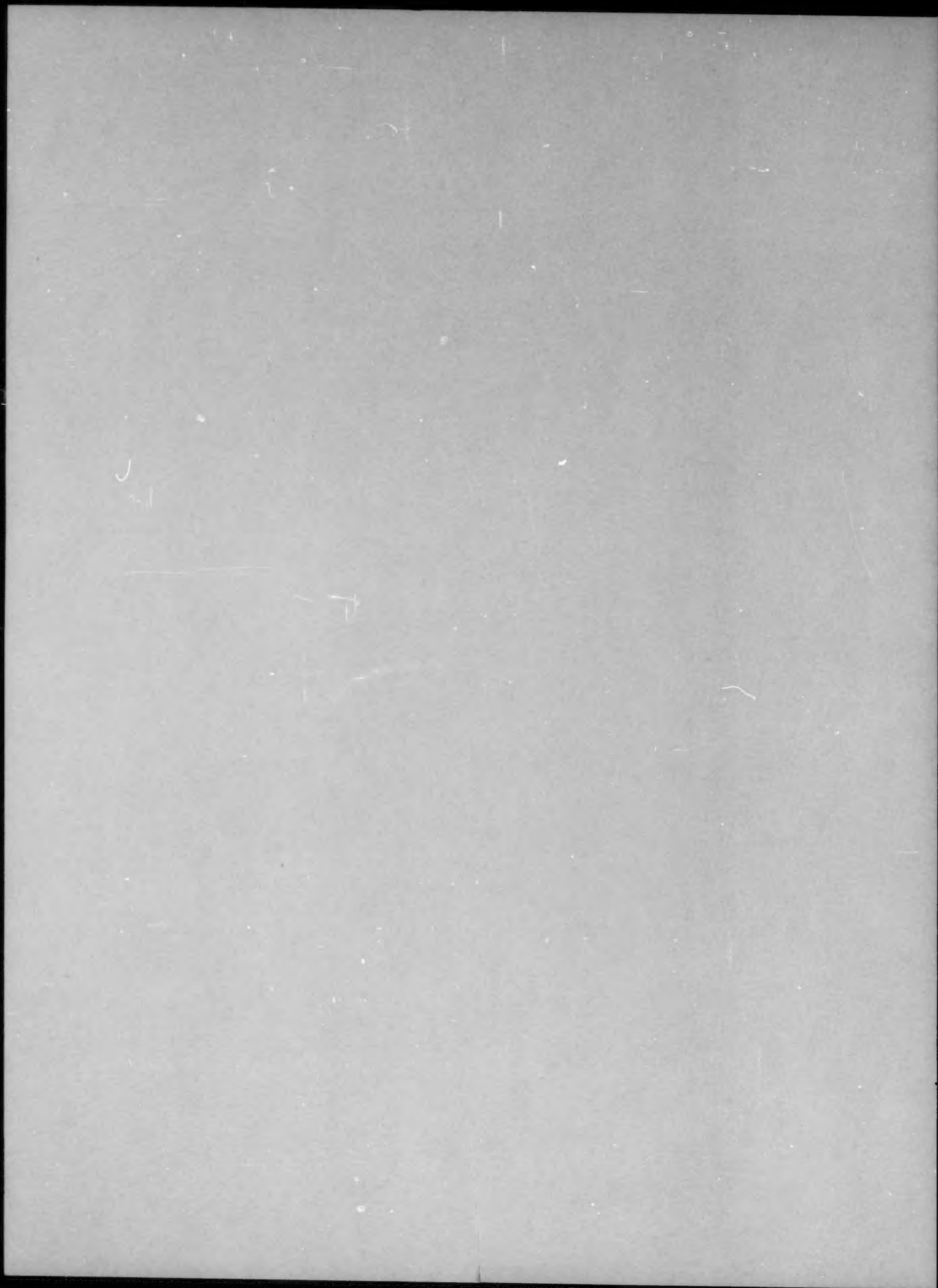BULLETIN OF ACADEMY
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PERIODICITY IN THE STRUCTURE OF THE ELECTRON ENVELOPES

AND NUCLEI OF ATOMS*

COMMUNICATION 1. PERIODIC SYSTEM OF THE ELEMENTS AND ITS CONNECTION
WITH THE THEORY OF NUMBERS AND WITH PHYSICOCHEMICAL ANALYSIS

A. F. Kapustinsky

1. Introduction

The fundamental law of chemistry — Mendeleev's periodic law — is manifested in a great variety of ways. It is most intimately bound up with the theory of atomic structure, and the periodic system of the elements derived from it consists in the classification of atoms according to the structures of their electron envelopes. The electronic theory of atomic structure and valency could not have developed, and cannot continue to develop, without the direct and determining participation of the Mendeleev law and the Mendeleev system. The question of the structure of the periodic system of the elements has been the subject of numerous investigations, which we have referred to in a series of communications [1,2,3]. In these communications we have considered, in a concise but sufficiently detailed fashion, the facts and principles that must find their expression in a modern scheme of the system of elements. In the present paper, in our considerations of the structure of the periodic system arrived at in this way, we shall confine ourselves to such exposition of the structure as is necessary for the comprehension of a treatment in which we throw further light on the system by the use of number theory and physicochemical analysis.

The use of mathematics as a means of generalizing data obtained by experiment, which is so characteristic of modern chemistry, does not replace real physicochemical objects by fictitious, abstract mathematical concepts. The object in our inferences here, and in other fields of science (for example, that of the phase rule) which are concerned with definite numerical relationships, is to represent facts observed by chemists by means of geometric models, and also to describe them with the aid of the language of mathematics. It is quite obvious that the systematization and description of known facts with the aid of mathematical terms and method cannot and does not lead to anything more than that which experiment yields to the investigator.

2. Structure of the Periodic System of the Elements

The rational structure of the periodic system of the elements contains: a) a zero period and zero group of elements; b) a subdivision of the system into even and odd periods and into cycles, which express a secondary periodicity; c) an evolutionary representation of the nature of the elements (proto-elements → typical elements → elements "of complete structure"). In Fig. 1 a stepwise representation of the system is given. In this the black spots represent elements of the even periods and circles represent those of the odd periods. The numbers of elements in the periods and in the cycles, each of which consists of a pair formed by an even and an odd period, are given below the diagram. The system is complete up to centium (z = 100). The same can be expressed by means of a network of cells (Fig. 2). The bold line represents a discontinuity; the cell occupied by hydrogen rests simultaneously on cells of groups I and VII. In the left part of the diagram the periods and cycles are given; and below the actinides and lanthanides are shown. The detailed derivation of these representations of the system, as also the arguments relating to the necessity of introducing the electron (e) and the neutron (r) into the system, is not given here (see [3]). We will add that in the table in Fig. 2 atomic weights are given and the recently discovered elements Athenium (An) and Centium (Ct) are included (as also in Fig. 1. The 6d shell is completed at element 104**.

$S = 4 \cdot n^2$

● e ─── o 1 H
● a ─── o 2 He

● 3 Li ─── o 11 Na
● 4 Be ─── o 12 Mg
● 5 B ─── o 13 Al
● 6 C ─── o 14 Si
● 7 N ─── o 15 P
● 8 O ─── o 16 S
● 9 F ─── o 17 Cl
o 10 Ne ─── o 18 Ar

● 19 K ─── o 37 Rb
● 20 Ca ─── o 38 Sr
● 21 Sc ─── o 39 Y
● 22 Ti ─── o 40 Zr
● 23 V ─── o 41 Nb
● 24 Cr ─── o 42 Mo
● 25 Mn ─── o 43 Tc
● 26 Fe ─── o 44 Ru
● 27 Co ─── o 45 Rh
● 28 Ni ─── o 46 Rd
● 29 Cu ─── o 47 Ag
● 30 Zn ─── o 48 Cd
● 31 Ga ─── o 49 In
● 32 Ge ─── o 50 Sn
● 33 As ─── o 51 Sb
● 34 Se ─── o 52 Te
● 35 Br ─── o 53 J
● 36 Kr ─── o 54 Xe

● 55 Cs ─── o 87 Fr
● 56 Ba ─── o 88 Ra
● 57 La ─── o 89 Ac
● 58 Ce ─── o 90 Th
● 59 Pr ─── o 91 Pa
● 60 Nd ─── o 92 U
● 61 Pm ─── 93 Np
● 62 Sm ─── o 94 Pu
● 63 Eu ─── o 95 Am
● 64 Gd ─── o 96 Cm
● 65 Tb ─── o 97 Bk
● 66 Dy ─── o 98 Cf
● 67 Ho ─── o 99 An
● 68 Er ─── o 100 Ct
● 69 Tu ─── o 101
● 70 Yb ─── o 102
● 71 Cp ─── o 103
● 72 Hf ─── o 104 (Eka Hf)
● 73 Ta ─── o 105
● 74 W ─── o 106
● 75 Re ─── o 107
● 76 Os ─── o 108
● 77 Ir ─── o 109
● 78 Pt ─── o 110
● 79 Au ─── o 111
● 80 Hg ─── o 112
● 81 Tl ─── o 113
● 82 Pb ─── o 114
● 83 Bi ─── o 115
● 84 Po ─── o 116
● 85 At ─── o 117
● 86 Rn ─── o 118 (Eka Rn)

$n_1 = 1$ $n_2 = 1$ $n_1 = 2$ $n_2 = 2$ $n_1 = 3$ $n_2 = 3$

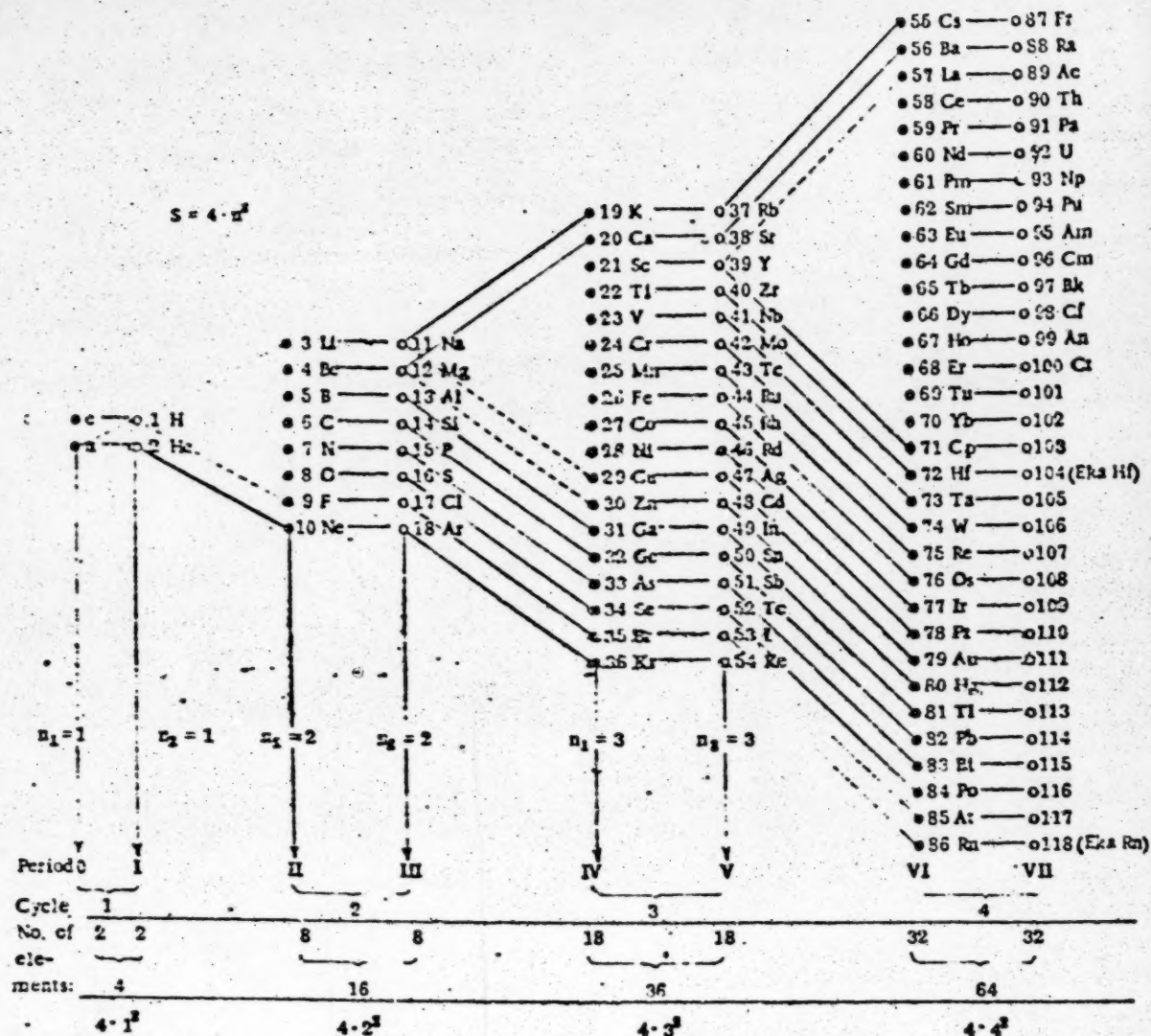| Period	0	I	II	III	IV	V	VI	VII
Cycle	1		2		3		4	
No. of elements:	2	2	8	8	18	18	32	32
	4		16		36		64	
	$4 \cdot 1^2$		$4 \cdot 2^2$		$4 \cdot 3^2$		$4 \cdot 4^2$	

Fig. 1. Stepwise representation of the system

and at the end of the system is an atom of the inert-gas type belonging to the zero group, which it would be correct to call ekaradon (EkaRn). Altogether, there are 18 elements that have still not been discovered: from centum (100) to ekaradon (118). There can be no doubt that in their preparation, as also in their investigation, Mendeleev's law will play the same leading part as it has played up to the present.

3. Periodicity of the Properties of the Elements, and the Theory of Numbers

There can be no doubt that it is in the theory of numbers that we find the best way of describing the periodic law and the periodic system in mathematical terms, for this branch of mathematics concerns itself with discontinuous quantities. Although Mendeleev pointed this out more than half a century ago [5], there have been no systematic attempts to apply the theory of numbers in chemistry.

D. I. MENDELEEV'S PERIODIC SYSTEM OF THE ELEMENTS

Cycle	Period	Series	GROUP								
			1	2	3	4	5	6	7	8	0
1	0	0				e					n
	1	I			H						He
2	2	II	Li	Be	B	C	N	O	F		Ne
	3	III	Na	Mg	Al	Si	P	S	Cl		Ar
3	4	IV	K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni	
		V	Cu	Zn	Ga	Ge	As	Se	Br		Kr
	5	VI	Rb	Sr	Y	Zr	Nb	Mo	Tc [99]	Ru Rh Pd	
		VII	Ag	Cd	In	Sn	Sb	Te	I		Xe
4	6	VIII	Cs	Ba	La •	Hf	Ta	W	Re	Os Ir Pt	
		IX	Au	Hg	Tl	Pb	Bi	Po [210]	At [211]		Rn
	7	X	Fr [223]	Ra	Ac ••						Eka Rn
		XI	—	—	—	—	—	—	—		

LANTHANIDES

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

ACTINIDES

Ac	Th	Pa	U	Np	Pu [239]	Am [241]	Cm [242]	Bk	Cf	An	Ct			

• Lanthanides   •• Actinides

Fig. 2.

The use of mathematics in chemistry is possible on account of the correlation principle, which establishes the correspondence of mathematical forms and their transformations with physicochemical objects and the changes that they undergo. Therefore, we shall first establish corresponding chemical and mathematical concepts for examination. Kurnakov [6], in writing that "the law of constant and multiple proportions is an application of the study of whole numbers to chemistry", shared the views of Kummer [7] according to whom "chemistry and the theory of numbers have as their principle — although in different spheres of activity — the same concept of composition". Composition in chemistry

Is expressed with the aid of the concept of element, and an element is a form of material to which a definite place in Mendeleev's system corresponds. This definition is in complete accord with that proposed by Kedrov [6]: "an element is a species of atoms that occupy one definite place in Mendeleev's system".

In the system, the cell, which is denoted by a serial number (the atomic or Mendeleev number), is the element's "passport", characterizing its individual nature. Thus, to the number concept in mathematics there is a corresponding concept in chemistry of atomic, or cell number.

Among all the kinds of periodic relationships in chemistry, the most perfect and all-embracing is the system of elements. Can there be among the various mathematical functions one that could express the extremely high degree of organization and interrelationship of discontinuous quantities, that would have a dual character, expressing in itself the interaction of these quantities and the unity of their opposing characteristics; that would be constructed on the basis of the periodicity concept, not in the sense of simple repetitivity, but a concept of periodicity in its evolution at ever higher and higher levels, although in the form of an abstraction —a form that expresses in itself the transition from quantity to quality —a function that itself determines the composition of the groupings that arise ?

Number theory enables us to give an answer to this question. Let us suppose that we have the natural series of integers from 1 to 120 (the basis for the upper limit will be given later):

$$1, \ 2, \ 3, \ 4, \ 5, \ 6, \ 7, \ 8, \ 9 \ldots\ldots\ldots\ldots\ldots 120.$$

In this series particular sets of numbers show various forms of periodicity, as may be seen, for example, for the Bernoulli numbers: the repetitivity may vary greatly. Which of the possible solutions corresponds to the criteria given above ? We may first of all eliminate the variant of simple mechanical repetition, for the main requirement is the possibility of repetition that includes in itself evolution, i.e., that continually passes to a higher and higher level. This requirement corresponds to the next in order of reducing simplicity after the natural series: the series of squares of even numbers, $2^2, \ 4^2, \ 6^2, \ 8^2\ldots$, i.e., 4, 16, 36, 64.... We then have a periodicity of defined number cycles, which grow regularly as we move from the beginning of the series, thus satisfying the requirement given above.

The solution would remain incomplete if the concept of composition, so important from the chemist's point of view, were not expressed in it. According to the theory of numbers [9], every integer has at least two factors: itself and unity. A number having only two factors is prime, and one having more factors is composite. In the natural series of numbers 4 is the first and simplest composite number. Hence, the question of the composition of groupings of numbers developing cyclically in the natural series is equivalent to the question of repetitivity, in conformity with rule, of the simplest composite number, i.e., four, both as a beginning and as a basis. It has a simple and unequivocal solution, for the sets of numbers given above consist in an n^2-times repetition of four. In fact, every one of them is expressed by the formula $4 \cdot n^2$, where n is the number of the given grouping obtained by counting in order from the beginning of the system. Thus, the series of natural numbers contains growing cycles, each having S members and conforming to an extremely simple expression, which is not equivalent to other axioms, or theorems, and which is intimately bound up with the mathematical concept of composition, namely:

$$S = 4 \cdot n^2.$$

By giving n the values 1, 2, 3, 4 we find that S becomes 4, 16, 36, 64. This expression is symmetrical and is in accord with the criterion of evenness and, in fact, duality.

The symmetry can be expressed by the condition stating that if the basis of the system is four, then its number of terms is also four. We then obtain a system of numbers:

$$4 \cdot 1^2 + 4 \cdot 2^2 + 4 \cdot 3^2 + 4 \cdot 4^2 = 120.$$

The evenness and dual character of this system permit us to break down each cycle into two halves. We have an analogous picture in a wave, which is composed of two half-waves. We shall call them number periods. According to definition, the number of numbers in the periods (which combine in pairs into cycles) will be (in order):

$$2, 2, 8, 8, 18, 18, 32, 32.$$

The system under consideration, therefore, forms itself into two number "rays" of periods —even and odd (according to the serial number of the period). Let us consider the results so obtained. With the aid of the theory of numbers and by an examination of the regularities found in the series of integers 1, 2, 3, 4, 5, 6 ......120, we conclude that within the limits of such a series.
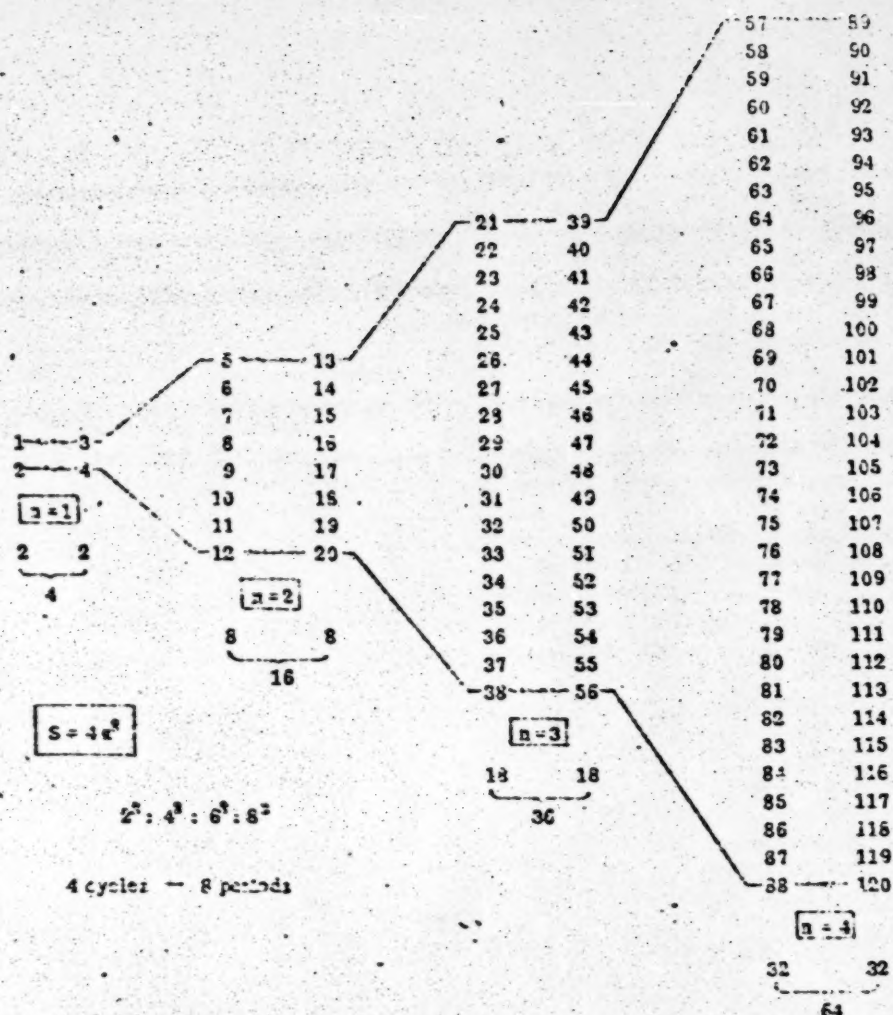
Fig. 3. Number system for n^2-times repetition of the simplest composite number.

a) there is a periodicity expressed by the set of numbers 1, 2, 3, 4, 5, 6 ....120;

b) the periods combine in pairs, each comprising an even and an uneven period, containing groupings of 4, 16, 36, 64, which conform to the law of an n^2-times repetition of the simplest composite number.

Such a mathematically derived concept of periodicity includes not only repetitivity of definite groupings (n^2-times repetition of the simplest composite number, (four), but also the growth of cycles as they evolve; it expresses also the dual character and symmetry of structure of the system of numbers obtained — a structure formed by two — even and uneven — rays of periods. It is not difficult to see that we have satisfied all the requirements of a mathematical representation of the periodic system of the elements, the starting point for which is the correspondence between the concept of element in chemistry and that of number in mathematics, as formulated by us at the beginning. There only remains the final step of constructing a series of numbers from 1 to 120 following the results of the mathematical analysis of periods obtained above (Fig. 3).

A comparison of Figs. 1 and 3 confirms the complete identity of the periodic system of numbers with the variant we have developed of Mendeleev's periodic system. The structures of the two systems are identical. All parts of the two systems, in agreement with the correlation principle, compared with one another: a) number

element. b) "half-wave" or number period — period of the system of elements; c) number cycle —cycle of the system of elements, which combines within itself an even and an odd period.

It is obvious, of course, as we emphasized at the very beginning, that we have here a correspondence, not an identity. There is no simple equality between a mathematical number and a Mendeleev number. The former gives a formal ordinal number in the system, and the latter, in as much as the first two elements, the electron and neutron, have zero Mendeleev numbers, is equal to the nuclear charge. However, even the electron and the neutron, being individuals, correspond in the mathematical system to numbers (1 and 2). For this reason there is a displacement by two places in the succession of "chemical" numbers in comparison with the "mathematical" numbers, a circumstance that is without fundamental or practical significance for the mathematical expression of the periodic system of elements. What, then, is the physical meaning of the numbers that run like a red thread through the system under consideration, i.e., 2 and 4?.

First of all, it will be noted that 2 is the two possible values of the spin, and 4 is the four quantum numbers s, p, d, and f. But the most general and therefore the most correct explanation is that 2 expresses the dual character of the system of elements and the simplest composite number 4 is the number of proto-elements (electron, neutron, proton, α-particle), which lie at the basis of the system and enter into the composition of the atoms of the remaining elements. All that we have expounded here, of course, is applicable both to the evolutionary and to the cell representation of the system.

The concept of "system" is wider than that of "periodic law" in its generally accepted formulation. It is true that a mathematical analysis of its structure indicates an exact correspondence between the system and the law of the periodic dependence of properties on the place occupied by the element in the system (Mendeleev periodicity), but that is not all. It emerges very strikingly from the system that the periods themselves, being repeated in a cyclic fashion, exhibit a "periodicity of periods", or secondary periodicity, which was first discovered by Biron [10]. It is not expressed at all in Mendeleev's formulation of the law and is closely associated with the general structure of the system in accord with the results of experimental chemistry [2].

What we have given above is not a mathematical derivation of the periodic system of elements. It is impossible to derive a real physical law from abstract numbers. Also, the correspondences that we have established are in no way intended as a replacement of the periodic law, in all its variety, by simple mathematical equations; they are intended to throw light on one part, although it is a very important part, of the problems relating to the structure of the system of elements. We are concerned only with the mathematical expression of experimentally found generalizations, but this is indeed a step toward the goal of Mendeleev —the discovery of an exact expression of the periodic law and of the periodic system of elements.

4. Physicochemical Analysis and Geometry of the Structure of the Mendeleev Periodic System of Elements

Graphical representation of various physicochemical systems and processes is widely used in general and physical chemistry. It has found its widest application in Kurnakov's physicochemical analysis, which brings together chemistry and geometry on the basis of correlation principles and of the continuity of transformations, and which enables us to make a new approach to the concept of the chemical individual.

It is possible that further development of the study of singular points in composition—property diagrams will reveal new methods for the graphical interpretation of Mendeleev's periodic law, in as much as the correspondence of any individual (daltonide) to a singular point coincides with the correspondence of an element —which is a chemical individual — to the concept of a special point in geometry. At the present time, however, at least without fundamental changes in the basic principles of physicochemical analysis, it is impossible to count on success in this direction.

The reason for this is that the method of physicochemical analysis, which can be successfully extended to any composition—property diagrams whatever, is strictly based on thermodynamical principles, as Kurnakov emphasized [6]. There is good reason why the main concept with which it operates should be the concept of a phase, homogeneous and continuous, as defined by classical thermodynamics. This is closely related to the fact that the principle of continuity of transformations occupies the foremost place in the theory of physicochemical analysis. The main laws, obtained in strict fashion by the use of above-described concepts, are extended further to non-equilibrium systems and non-thermodynamical properties.

However, neither the concept of the phase nor the principle of continuity of transformations is applicable to the analysis of the periodic system of the elements. In the first place the periodic system is a system of atoms. It relates essentially to isolated atoms and also has no specific character such as is peculiar to statistical assemblies, i.e., phases, and is therefore like any generalization relating to the structures of atoms and molecules. In the second place, at least in the available range of temperature and pressure, there are no states of equilibrium and continuous transformations between the various elements; the periodic law cannot therefore be expressed with the aid of continuous functions. Hence, the geometry of the structure of the periodic system of elements must also be the geometry of discontinuity. Here lies the essential difference from the usually applicable methods of physicochemical analysis. In all other respects, however, the ideas upon which Kurnakov based the theory of composition—property diagrams are quite applicable to the solution of the question of the geometrical representation of the structure of the periodic system of elements.

In accord with the correspondence principle, the concept of the element in discontinuous geometrical figures has its counterpart in the elementary square or cell. The next concept in complexity, the period, corresponds to a parallelogram (rectangle); the number of cells that it contains, which is equal to its area, is the number of elements in the period. Two contiguous periods (even and odd) taken together form a single cycle of the system. Thus, the geometrical counterpart of the cycle in the system of elements is the square, which is composed of two rectangles (right and left); its symmetry is expressed in its square outline, and the number of cells that it contains, which is equal to the number of elements, is therefore determined by the quadratic expression: $S = 4n^2$, where n is the series of integers.
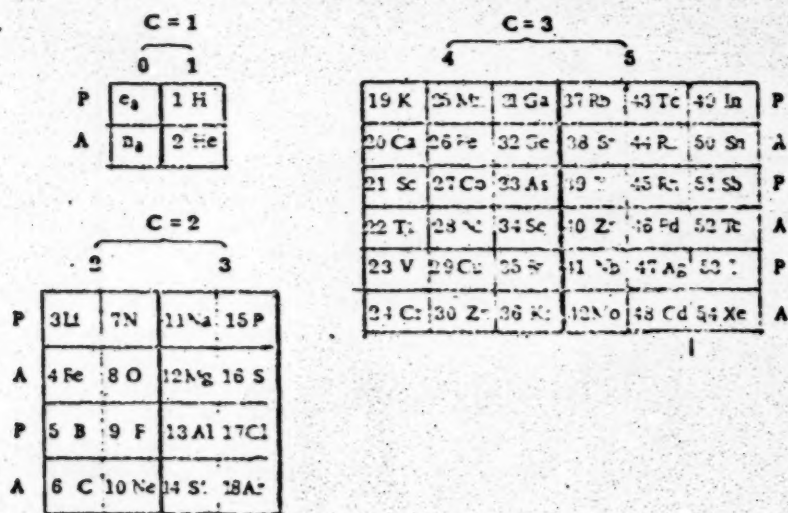

Fig. 4. Representations of cycles.

Starting from this correspondence of elements and structural parts of the periodic system with discontinuous geometrical forms, we can construct the corresponding representations for each of the cycles (Figures 4 and 5). In each square the cells corresponding to the elements are disposed in the order of the Mendeleev numbers of the elements. The "anisotropy" of each square consists in the fact that even and odd numbers (Mendeleev numbers) are brought together in alternative horizontal rows, thus bringing together Shchukarev's artiads and periads [11] (denoted by A and P). Above each square the number of the cycle (C) is given, and above each rectangle, the number of the period.

It will be seen from the number of variables under examination that the system cannot be completely represented on a plane; it can be represented only in three-dimensional space. A three-dimensional figure containing squares in the form of sections parallel to the base separated by distances proportional to the capacities of the cycles is to be found in a truncated tetragonal pyramid (fig. 6), which has a symmetry that is characteristic of the structure of Mendeleev's periodic system of elements and which consists of two halves, related symmetrically as in mirror images, which are assigned to even and odd periods, respectively.

Fig. 5. Representation of a cycle.

	C = 4						
	6	7					
P	55 Cs	63 Eu	71 Cp	79 Au	87 Fr	95 Am	103	111
A	56 Ba	64 Gd	72 Hf	80 Hg	88 Ra	96 Cm	104	112
P	57 La	65 Tb	73 Ta	81 Tl	89 Ac	97 Bk	105	113
A	58 Ce	66 Dy	74 W	82 Pb	90 Th	98 Cf	106	114
P	59 Pr	67 Ho	75 Re	83 Bi	91 Pa	99	107	115
A	60 Nd	68 Er	76 Os	84 Po	92 U	100	108	116
P	61 Pm	69 Tu	77 Ir	85 At	93 Np	101	109	117
A	62 Sm	70 Yb	78 Pt	86 Rn	94 Pu	102	110	118

Fig. 6. Spatial representation of the system.

Fig. 7. Projection on the base of the spatial representation of the system.

This three-dimensional form of representation can be projected onto the base. The figure so obtained also presents a geometric expression of the structure of the periodic system of elements (Fig. 7). In the examination of this diagram, as also of the previous ones, it must be remembered that it is concerned with the geometric representation of the system and is not intended to replace in any way the evolutionary and tabular forms of the system (see Section 2).

In the geometric form given in Fig. 7, the interrelations of elements, periods, cycles, and (along the diagonal) groups are presented. The boundaries of the cycles are indicated by bold lines. All other indications are given directly on the figure. Such a diagram enables the interrelationship between all the concepts used in the construction of the periodic system to be represented in an extremely graphic fashion.

Just as, according to Kurnakov [6], any composition — property diagram is a closed complex, so in the diagram that we have advanced for the periodic system of the elements we find, using the word in the same sense, a closed diagram.

The geometric interpretation of the periodic system is in complete accord with the representation of the system in terms of number theory. "The system presents itself to us as a unified whole, harmoniously developed and having a regular and logical structure, answering in spirit and sense the designation "system"; its fundamental completeness is evident; it is incomplete only with respect to the discovery of new elements, in the effecting of which it will form, as it has done in the past, a leading thread in the investigations. All that we have expounded above will help in the realization of Mendeleev's goal: to give mathematical representations of the system with the aid of number theory and the geometry of discontinuous quantities.
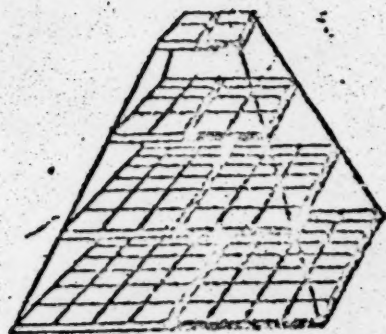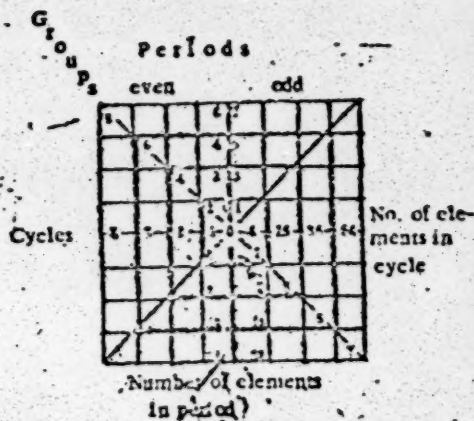
SUMMARY

1. A horizontal, cell-form representation of the periodic system of elements is given in which

a) a zero period (electron, neutron) and zero group (neutron, He, Ar, Ne, Kr, Xe, En, ekaradon) are included;

b) subdivision is into periods and cycles expressing secondary periodicity;

c) there is a hydrogen "cell" adjoining Groups I and VII.

2. It has been shown that the structure of Mendeleev's periodic system can be described with the aid of number theory; and Kurnakov's physicochemical analysis is applied to the geometric representation of the periodic system.

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PERIODICITY IN THE STRUCTURE OF THE ELECTRON ENVELOPES AND NUCLEI OF ATOMS

COMMUNICATION 2. CLASSIFICATION OF THE ATOMIC NUCLEI OF THE ELEMENTS ON THE BASIS OF THE PACKING EFFECT AND THE LAYERED STRUCTURE OF THE ATOMIC NUCLEUS

A. F. Kapustinsky

1. Introduction

The exceptional progress made in the experimental chemistry and physics of the nucleus has not been accompanied by corresponding developments in the theory of nuclear structure. Although Ivanenko's proton-neutron theory is generally acknowledged, in detailed investigation recourse still has to be made to mutually inconsistent concepts, each of which is generally confined in its application to the solution of a special group of questions. Such nuclear models are: 1) those composed of independent particles, 2) similar to 1), but a closer approximation (Hartree), 3) those built from helions, 4) analogs of a solid, 5) analogs of a liquid drop. Fermi [1] has recently remarked that "different nuclear models give good descriptions of different peculiarities of the nucleus; no single one of the simple models accounts for all the properties of the nucleus". Devons [2] also is not inclined to be optimistic; he asserts that "it may be said of many, if not of most, of the existing experimental data, that they are in very poor agreement' with theory". It would not be an exaggeration to assert that there is no general, single point of view consistent with the various experimental data to the extent found in the theory of electron envelopes of atoms. At the present stage of investigation – the stage concerned with the search for a general theory – it is useful, and even essential, to compare the various experimentally established properties of nuclei, to attempt to establish the quantitative relationships, even although they may be approximate, that are to be found, and to develop the corresponding schemes of classification and structural models — to do all, in fact, that can serve to further, widen, and intensify the investigation of this problem.

It must be said that this is indeed the direction followed in investigations by Spytsyn [3], Selinov [4], Sarkisov [5], Cherdyntsev [6], Zhdanov [7] and others.

These investigations have revealed the undoubted existence of periodic relationships in the nucleus and have shown that the periodic properties may be of a most varied kind; the nuclear periodicities found, however, do not in any way form a simple repetition of the periodicity of the electron atmosphere.

In the present paper (see also Communication 1), we have tackled the problem of analyzing the possibility of the existence of a periodicity corresponding to a layered structure in the nucleus and of bringing it into relationship with Mendeleev's law.

2. Rectilinear-Diameter Rule for the Packing-Effect Curve

In the theory of atomic structure an essential part is played by the examination of the curve for the packing effect, which permits the relative stabilities of nuclei to be compared. This smooth curve, however, has not been subjected to a mathematical analysis capable of relating together the characteristic quantities by which its position within the system of coordinates is determined: the packing effect m and the atomic number z (Fig. 1). However, by carrying out this analysis, we may, as will be shown below, not only relate this curve to analogous curves expressing other physicochemical functional relationships, but also arrive at certain generalizations essential to the classification of atoms.

Let us consider the most characteristic atoms for each element, namely, the isotopes that are most stable and most abundant in nature. It is to them, essentially, that our inferences will apply. Let us point out at once the exceptional position of beryllium, which, as Cherdyntsev emphasized [6], has as its most abundant isotope, Be_4^9, in spite of the general rule of the greater abundance of even isotopes (abundance of Be_4^9 is 0.05 %).
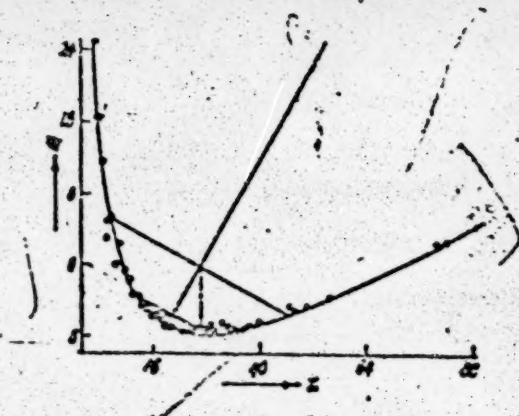
Fig. 1. Dependence of packing effect m on the atomic number z for the most abundant isotopes of the elements.

Fig. 1, which is constructed from compiled data [8], represents the relationship between the packing effect m and the atomic number (Mendeleev number) z, and not the mass number (the usual procedure). The evident symmetry of this curve prompted us to apply the method of analysis first developed for physicochemical curves of this type by Alekseev [9], who established the law of rectilinear diameter for the mutual solubility of liquids. A similar law was used by Cailletet and E. Mathias [10] for finding critical volumes.

We have drawn the curve in Fig. 1 so that its two branches are strictly symmetrical with respect to the rectilinear diameter passing through the vertex of the curve. The experimental values of the packing effect (Fig. 1) either coincide with the curve drawn in this way, or depart from it to an insignificant extent. We may remark that the departures are here less than for such classical examples of the application of the rule of rectilinear diameter as the systems carbon disulfide— methanol and triethylamine — water. Also, let us, following the custom for the rules of Alekseev —Cailletet—Mathias, call the lines perpendicular to the diameter and uniting corresponding points of the two branches of the curve by the name of conodes.

From an examination of Fig. 1 we come to the following conclusions:

a) The rectilinear diameter passes through a characteristic point, the vertex of the curve, corresponding to atomic number 20 (calcium). The isotope Ca_{20}^{40} is characterized by the equality of the numbers of the three component parts of the atom: 20 electrons, 20 protons, 20 neutrons. This first characteristic point we shall call the critical point of the packing-effect curve.

b) The upper branch of the curve refers to atoms of elements standing before calcium in Mendeleev's system. Their general property is the equality in number of protons and neutrons; only for certain isotopes of maximum abundance (lithium, fluorine, sodium) is there an extra neutron. We shall call such atoms that are homogeneous with respect to number of protons and neutrons by the name of homonucleons, and the upper branch that corresponds to them — the homonucleon branch.

c) The lower branch refers to atoms of elements standing after calcium. For these, the further we go, the more the number of neutrons exceeds the number of protons. We shall call such heterogeneous atoms by the name of heteronucleons and the corresponding section of the curve — the heteronucleon branch.

The above treatment enables us to arrive at a generalization, which may be called the rectilinear-diameter rule for the packing-effect curve (in coordinates of packing effect against atomic number): the packing-effect curve is a geometric locus of points equidistant from a rectilinear diameter passing through the critical point of the packing effect (Ca_{20}^{40}).

Another formulation of the rule, equivalent to the above, is as follows: the locus of the centers of conodes drawn through figurative points of the homonucleon and heteronucleon branches is a straight line passing through the critical point of the packing effect, $z = 20$ (Ca).

The equation of the rectilinear diameter for this case is:

$$\frac{m_1 + m_2}{2} = 0.85z - 22, \tag{1}$$

where m_1 and m_2 are corresponding figurative points (homonucleons and heteronucleons at the ends of the same conode).

Passing now to an examination of the electron envelopes of homonucleon atoms and heteronucleon atoms,

we find that the atoms of all elements standing before calcium in Mendeleev's system have only s- and p-electrons, whereas those following calcium may have s, p, d, and f electrons. This may be represented as follows (Table 1):

TABLE 1

Nuclear characteristics	Homonucleons	Critical point of the packing-effect curve	Heteronucleons
Electronic characteristics	s,p-electrons	Ca_{20}^{40}	s,p,d,f-electrons

After an examination of the result obtained, it is impossible not to reach the conclusion that there is a definite correlation between the structure of the electron envelope and the type of nuclear composition.

We have considered the first characteristic point. We shall now show that the curve under analysis has a second characteristic point. Since the rectilinear diameter is not perpendicular to a coordinate axis, the packing effect curve must have a minimum, at which the derivative of m with respect to z changes sign. We shall call the minimum point the second critical point of the packing effect curve; its value may be found both directly from the graph (Fig. 1) and also by the aid of Equation 1. Actually, for the zero connode (i.e. that intersecting the zero level of the packing effect):

$$\frac{m_z + m_A}{2} = 0 \tag{2}$$

Substituting from Equation 2 in Equation 1, we obtain the same result as that given directly by finding the minimum from the graph (Fig. 1), namely $z = 26$. This is the atomic number of the element corresponding to these minimum conditions, namely iron.

Among all the possible connodes there are two of particular significance: the zero connode

$\frac{m_1 + m_2}{2} = 0$ just described, and the minimum connode, passing through the minimum of the curve $(z = 26)$.

They are not unrelated, on the contrary, as will be seen from the figure, they are related to one another: the perpendicular from the lower end of the minimum connode $(z = 26)$ passes through the center of the zero connode. They form, therefore, a unified system. The four points corresponding to these connodes are special points on the packing effect curve; their values — $z = 6$, 12, 26, 46 — are the atomic numbers of carbon, magnesium, iron, and palladium. As is well known, one of the forms of expressing Mendeleev's periodic law is the curve of atomic volumes. It is these four elements that occupy the minimum positions on this curve; they are in the central positions in the corresponding periods of Mendeleev's system. We see that all four special points of the packing effect curve belong to atoms of minimum volume in the periodic system, and since the atomic volumes are determined by the dimensions of the electron atmospheres of the nuclei, we again conclude that close correspondence must exist between the nuclear characteristics of an atom and the electron atmosphere of its nucleus.

3. Homonucleon and Heteronucleon Nuclei

The analysis that we have given of the packing-effect curve is only the first rather crude approach to the solution of the general problem of the correspondence between the properties of the nucleus and of the electron envelope; it considers neither the question of even and odd atomic numbers, nor the finer points concerning the existence of isotopes, nor the tendency of atoms to undergo disintegration of various types. It permits us, however, to make a significant step forward, for it tells us of a quantitative relationship, the law of the rectilinear diameter, which brings the characteristic points of the packing-effect curve into relation with the minimum points of the curve of atomic volumes, and also brings nuclear characteristics into relation with the characteristics of the electronic atmosphere of the atom.

It is necessary to consider the division of the atoms of the predominating isotopes of the elements into homonucleons and heteronucleons in more detail. Although it is not of an absolute character (see, for example, Be_4^9), it gives a classification of elements that is correct in its main features from the point of view of the nuclear theory of the nucleus, and it again emphasizes the special part played by calcium (Ca_{20}^{40}).

From this point of view it is doubtful whether it is possible to draw a single curve having z and the ratio of the numbers of protons p and neutrons n as its coordinates. It would be more natural to regard it as consisting of two different branches: one relating to homonucleon elements, and the other to heteronucleons, the equation (3) established by Spitsyn [11]:

$$\frac{n}{p} = 1.13 + 0.057 \cdot z \qquad (3)$$

being regarded as applying to heteronucleons.

It is of interest to examine in greater detail the course of the changes in the numbers of protons and neutrons in the nucleus as the atomic number z increases. As will be seen from Fig. 2, this procedure gives only an approximate characterization of the atoms which permits, however, the establishment of quite definite boundaries between various types of nuclei. In this figure, which is based on compiled data [12] the numbers of protons (p) and neutrons (n) in the nucleus are given on the axis of ordinates, and the number of protons (i.e. the atomic number z) on the axis of abscissa for the atoms of Mendeleev's system (the most abundant, the most stable, or those having the greatest half-life). With these coordinates curve 1 is, of course, a straight line (the proton line). The points on curve 2 represent numbers of neutrons. Here the division of nuclei into homonucleons and heteronucleons will be clearly seen. As is well known, the number of actinides is considered to be equal to the number of lanthanides, and the curves can be continued only to the supposed end of the Mendeleev system (p = 115). Fig. 2 (Curve 2) clearly indicates the presence of three breaks in the smooth course: around lithium and beryllium (p = 4), calcium (p = 20), and lanthanum (p = 56), which, according to the α-particle model, correspond to numbers of particles of 2, 10, 23, and 60 (at the end of the curve)
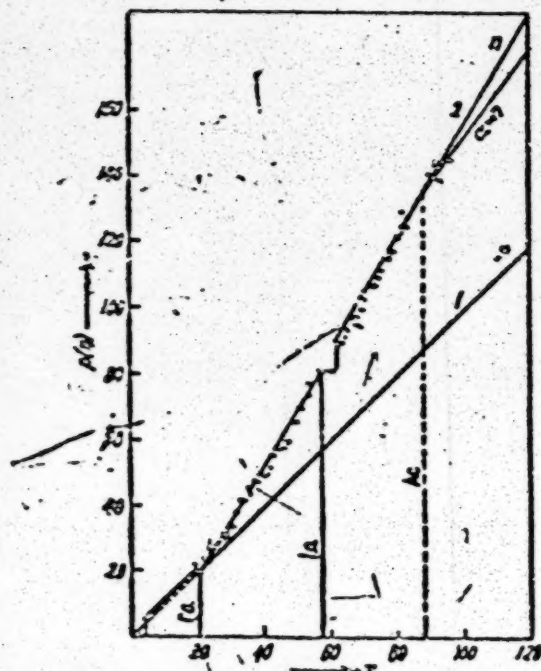
These breaks in the curves are not fortuitous and, in so far as we are concerned with nuclear properties, can be explained only by abrupt changes occurring in the structure of the nucleus in the course of its building up from nucleons. The following section of the paper is devoted to an attempt at such an explanation.

4. Periodicity in the Structure of the Nucleus Attributable to its Layered Structure

In the explanation of various properties of atoms, particularly in isotope chemistry, the most useful theory has been the α-particle hypothesis of nuclear structure, first stated by Rutherford in 1927 and later developed in various directions by Cherdyntsev [6], Spitsyn [13], Capon [14], Saxkisov [5], and other investigators. Starting from the basic ideas of this theory and regarding the α-particles in the nucleus as single particles formed by pairs of neutrons and protons, we may explain the breaks in the curve in Fig. 2 with the aid of the following hypothesis of the layered structure of the nucleus.

The so-called "Pauli exclusion principle", formulated in the first place with respect to electrons and later extended also to nucleons, was found to be inapplicable to α-particles, as also was Fermi statistics. Even if another method of theoretical physics is developed in the future which will permit the application of this principle to helions, or even if it is formulated in somewhat different form, there is still an evident need for the development of a theoretical method for the "selection" of particles according to their energy characteristics. It is of interest to attempt to apply this principle in its simple, noncomplicated form to the classification of helions. If we postulate that α-particles play the part of single particles in the nucleus and have energy characteristics given by a set of four

Fig. 2. Dependence of the numbers of protons p and neutrons n in the nucleus on the atomic number z of the most abundant isotopes

N	1	2	3	4
α	2	8	18	32
2	4	16	36	64

quantum numbers, analogous to the quantum numbers of electron chemistry, we arrive at results that are in good agreement with the facts presented graphically in Fig. 2.

If we assume that an exclusion principle analogous to that for electrons and nucleons is extended also to α-particles, we are in fact asserting that there cannot be two heltons in the nucleus having identical sets of four energy (quantum) characteristics. Calculating, in the manner usual in quantum theory, the number of possible groupings in each layer ("quantum level"), we obtain (see Table 2) the numbers of α particles in the first, second, third, and fourth layers, the resulting values being 2, 8, 18, and 32, corresponding to total numbers of heltons of 2, 10, 28, and 60, or to numbers of protons of 4, 20, 56, and 120, which coincide exactly with the atomic numbers of the elements corresponding to the breaks in Fig. 2a (Table 2).

Thus, the hypothesis of a layered helton structure is satisfactorily supported by the facts. It will be evident that nuclei have a four-layer structure: in the first layer there cannot be more than 2 α particles; in the second—not more than 8; in the third—not more than 18, and in the fourth—not more than 32.

TABLE 2

Quantum level	1	2	3	4
Number of α particles in each layer	2	8	18	32
Total number of α particles in nucleus	2	10	28	60
Total number of protons in the nucleus	4	20	56	120
Number of protons in nucleus corresponding to the breaks in the curve in Fig. 2	4	20	56	(120)
Number of protons in each layer	4	16	36	64

The layered nature of the nucleus is determined by its helton composition; the α-particles constitute, as it were, a "skeleton", the structure of which mainly determines the structure of the nucleus. The neutrons evidently play the part of binding particles, cementing the heltons together. As a result of the rapid growth of their number, already in actinium they become equal in number to the α-particles. It is possible that a structure then arises, similar to that of NaCl crystals, in which α and ν, alternating checkerwise in space, evenly and compactly fill the given volume. Such an arrangement is a limiting one: further increase in the "concentration" of neutrons renders the nucleus unstable. This feature, in fact, is characteristic of the transuranides (actinides). It may be considered that beyond the boundary indicated by the broken line in Fig. 2 an inflection will occur in the Curve 2, which will proceed as shown for α = ν. The tendency for the further accumulation of neutrons leads to a boundary at p = 118 at the end of the periodic system, and beyond this the existence of nuclei becomes energetically impossible. This does not, of course, exclude the existence of other, more complex forms of matter, for example, complex polynuclear formations analogous to polynuclear coordination compounds in the chemistry of complex compounds. But these stand outside the framework of the periodic system of the elements.

Although we find a layer in the structure of the nucleus corresponding to the lanthanides in the structure of the atom, the actinides do not correspond to the formation of a special layer, but to the onset of a condition of non-equilibrium between α particles and neutrons. The analogy between lanthanides and actinides, therefore, is incomplete, being the result of different causes. In fact, whereas the former are stable, the latter are characterized by unstable nuclei.

Here we again arrive at interesting comparisons between the structure of the nucleus and that of the electron atmosphere. In just the same way as the electron atmospheres of inert-gas atoms consist of complete stable layers, we have also complete stable layers of heltons in the nucleus (Fig. 3). The number of protons in these layers corresponds to the number of elements in paired groupings (cycles) of Mendeleev's system (4, 16, 36, 64), and the number of α particles that they contain corresponds to the number of elements in the periods (2, 8, 18, 32). The last question will be considered in the next section.

* An examination of the isotopic compositions of elements prompted Bethe and Bacher [15] and later Mayer, Nordheim, Haxel, and others, to suggest the presence of a series of closed proton-neutron shells in the nucleus. This suggestion will not be considered here, for their hypothesis of the presence of proton-neutron groupings in the nucleus containing 20, 50, 82, and 126 particles does not appear to have a sufficient basis and does not permit the systematic development of a theory of zonal nuclear structure directly related to the theory of the electron atmosphere of the atom. References to the literature on this question have been given by Duckworth [16].
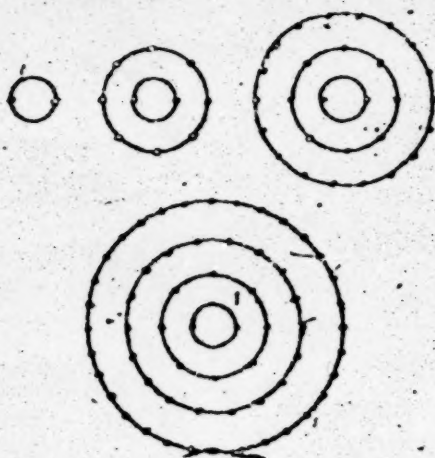
5. Relation of Nuclear Structure with the Structure of the Electron Envelopes of Atoms

This section is devoted to the question of the correspondence between the structure of the electron envelopes of atoms and the structure of the atomic nucleus. We shall compare the cycles and periods of Mendeleev's system, which are determined by the layered arrangement of electrons in the atom, with the periods of the nucleus, which are determined by the number of heltons (and also by the number of protons entering into their composition) in each layer of the nucleus. Table 3 gives the number of elements (which is equal to the number of electrons, since the atomic number is equal to the number of electrons in the atom) and the number of protons in the nuclear layer for each cycle (cf. Table 2).

Fig. 3. Periodic (layered) model of the atomic nucleus. The filling of the first, second, third, and fourth layers by α-particles.

TABLE 3

Cycle	1	2	3	4
No. of elements in cycle (No. of electrons)	4	16	36	64
Number of protons in the layer of the nucleus	4	16	35	64

The correspondence is so complete that comment would be superfluous. The cyclic character of Mendeleev's system of elements corresponds to the cyclic character found in atomic nuclei: 4 layers in the nucleus — 4 cycles in the system.

We shall compare now the number of elements in a period with the number of heltons in each layer of the nucleus (Table 4).

TABLE 4

Periods	0 and 1	2 and 3	4 and 5	6 and 7
Number of elements in period	2 and 2	8 and 8	18 and 18	32 and 32
Number of heltons in a layer of the nucleus	2	8	18	32

We see that each even and odd period contains a number of electrons equal to the number of heltons in a period of the nucleus. The results of these comparisons may be formulated as follows:

1. The cycles of Mendeleev's system of elements correspond to layers (cycles) of the nucleus, and the number of elements (electrons) in a cycle is equal to the number of protons in each helton layer of the nucleus.

2. The periods of Mendeleev's system are determined in pairs by the number of heltons in a layer of the nucleus.

There can be no doubt, therefore, in the following inference: the structure of the periodic system of elements, and therefore also the layered arrangement of electrons in the atom, stands in an exact, clear relationship with the structure of the system of atomic nuclei, with the layered arrangement of particles entering into the composition of the nucleus. It is possible that the structure of the electron atmosphere of the atom is determined mainly by nuclear forces, i.e., is determined by the structure of the nucleus.

Attention must be drawn to a characteristic peculiarity of the periodicity of the nucleus, which results from the fact that the composition of the nucleus differs essentially from that of the envelopes of atoms. Periodicity in Mendeleev's system is mainly the result of periodicity in the electron atmosphere, for it is on this that the chemical properties depend. Elements having electron atmospheres, however, begin only with hydrogen, i.e., they are delayed to the extent of two places (a zero period) behind the beginning of the system. This is the reason for there being

only a correspondence and not an identity in the characteristics of the periodicity of the nucleus and its atmosphere. "Chemical" (electronic) periods and my les begin always two places earlier than those in the nucleus. For example, that which begins for He_2 is connected in Ca_{20}; the previous layer of electrons ends at Ar_{18}, and only after two places does the completion of the helion layer occur (at Ca_{20}^{40}), after which a new layer begins in the nucleus*. The same occurs further on: Ba_{56} standing two places after Xe_{54}, is the boundary for the completion of the third layer of helions in the nucleus.

The internucleon forces in the nucleus are very powerful, and greatly exceed the weaker interactions that rule outside the nucleus. In the nucleus, therefore, we do not have incomplete levels and the completion of these levels. These finer nuances exist only in the electron atmosphere of the atom; they are peculiar to it, and there is evidently nothing that corresponds among the structural peculiarities of nuclei. This question, however, must be the subject of further investigation.

SUMMARY

1. A rectilinear diameter rule is proposed for the packing-effect curve. It states that this curve is the locus of points equidistant from a rectilinear diameter passing through the critical point of the packing effect (Ca_{20}^{40}). The equation for the rectilinear diameter in terms of the atomic number is given. It is shown that the characteristic points determining the position of the packing effect curve coincide with the minimum points of the atomic-volume curve.

2. With the aid of concepts of homonucleon nuclei (equal numbers of protons and neutrons) and hetero-nucleon nuclei (number of neutrons exceeds number of protons), the correspondence between the compositions of the nucleus and of its electron atmosphere is examined.

3. On the basis of an examination of the breaks in continuity on the diagram of number of nucleons plotted against atomic number, a hypothesis is advanced concerning the layered structure of the nucleus, the maximum number of helions in the layer being 2, 8, 18 and 36.

An attempt has been made to extend the "conclusion principle" to the helion model of the nucleus, in order to explain the existence of four layers of helions in the nucleus.

4. It has been established that a correspondence exists between the four cycles of Mendeleev's system of elements and the four layers in the structure of the nucleus and between the number of elements in the periods and the number of protons (entering into the composition of the helions) in the layers of nuclei. The periodicity in the structure of the electron envelopes is brought into relationship with that of the layers in the atomic nucleus.

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*It is interesting to note that the existence in the nucleus of a closed shell containing 20 neutrons and 20 protons (Ca_{20}^{40}) is predicted also by Hartree's method, as was shown by Wigner and Parkes [17].

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DETERMINATION OF THE STRUCTURE AND STRUCTURAL FORMULAS
OF ORGANIC COMPOUNDS FROM CRYSTALLOGRAPHIC DATA

G. B. Boky

1. There are a number of well known difficulties which the theory of the structure of organic substances has met in the field of aromatic compounds. For example, by the use of Kekule's model of the benzene nucleus it was found to be impossible to explain the absence of two ortho isomers among benzene derivatives and to dispose single and double bonds in a rational fashion in a whole series of aromatic compounds having condensed nuclei. As a result of these difficulties, organic chemists went to the other extreme and abandoned attempts to give exact representations of formulas by the aid of valency lines. In textbooks and scientific literature benzene rings began to be represented by simple hexagons, without any indication of the distribution of single and double bonds. This "leveling out" of bonds amounted to the recognition in benzene nuclei of only one type of bond between carbon atoms — intermediate between single and double.

If we employ the elementary electronic concepts widely used in organic chemistry and assign three valency electrons to each such bond, we can obtain a scheme for the structure of the benzene molecule. This scheme, however, cannot be used for representing the structures of naphthalene, anthracene, and other more complex substances. In the naphthalene molecule, for example, there are 11 bonds between carbon atoms, but the number of valency electrons remaining for their formation is 32.

The "leveling out" of all the bonds between carbon atoms in aromatic compounds is in conflict also with a number of recent experimental results on interatomic distances and the symmetry of organic compounds. These data are published mainly in special crystallographic journals, and often remain unknown to the majority of organic chemists.

2. The present stage of development in chemistry is associated with the appearance of the method of x-ray-structure analysis, which enables us to determine interatomic distances in molecules and radicals and thus introduce a quantitative element into the purely qualitative stereochemical concepts of classical chemistry. This demands consideration of the values of interatomic distances and, in particular, their influence on the chemical behavior of molecules.

It is impossible, however, to approach this question in a purely mechanical fashion and consider that each valency line in the formula always corresponds to the same interatomic distance in the structure of an organic compound. The mutual effects of atoms in molecules may bring about substantial changes in interatomic distances. The lengths of bonds between carbon atoms (or atoms of other elements) of identical multiplicity may have different values in different compounds, and even in one compound between different atoms. The length, however, of the bond between corresponding atoms in different crystals of the same compound has always a quite definite value.

First of all we shall consider the effect due to changes in valency angles. In 1944, when carrying out an analysis of the structure of PtS, we pointed out that, in spite of the great difference in electronic structure between platinum and sulfur atoms and the difference in the values and spatial arrangement of the valency angles, their deformations are approximately the same [1]. Kitaigorodsky had demonstrated the same idea with respect to pairs of molecules such as $CHCl_3$, CH_3Cl, and others having strictly tetrahedral valency angles.
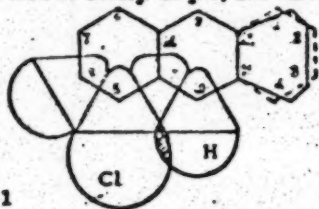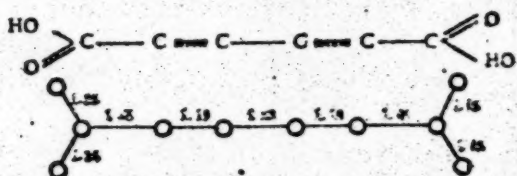

Fig. 1

Fig. 2.

In Fig. 1, the hydrogen and chlorine atoms are drawn to scale. The repulsion of chlorine and hydrogen atoms not united by a valency (at 6— and 10—C) is bound to result in the lengthening of the 10—13 bond.

The distortion effect in the valency angles will evidently be more marked at the edges of molecules and may therefore be called the "edge effect". Atom 1 will be repelled from atom 9, since it meets no resistance from the

opposite side (see Fig. 1); this will lead to lengthening of the bond 1—11 and shortening of the bond 1—2, accompanied by increase in angles 2 and 3 to values above 120° and decrease in angles 11 and 12. Shortening of the bond between atoms 1 and 2 may lead to the localization in this place of a double bond and therefore further reduction in the distance between these atoms.

The occurrence of single bonds between multiple bonds leads, as is well known, to their shortening. This effect is very much more marked than the interatomic-distance effects observed for atoms not united by valency. In particular, it has long been known that in paraffins and other aliphatic compounds a single bond has a length of the order of 1.54 A, or even somewhat greater than this. In aromatic compounds, however, the length of a single bond is not generally greater than 1.45—1.46 A. As an example of very considerable shortening of a single bond let us examine the results of the X-ray analysis of the dihydrate of butadiynedicarboxylic acid (Fig. 2) [2].

The distance between carbon atoms in the system $\equiv C - C \equiv$ is 1.33 A, instead of the usual 1.54 A in paraffins. It is less than the usual distance for a double bond C=C (about 1.35 A). This example shows that the length of a bond is not always an unequivocal characteristic of its multiplicity. Naturally, the properties of the bond will change also, if its multiplicity is maintained but its length considerably altered. Sometimes bonds of equal length must be assigned differing multiplicities, and in special cases it is conceivable that the shorter bond may have a lower degree of multiplicity. These, of course, are exceptional cases. In the general case, however, other things being equal, shorter interatomic distances correspond to higher multiplicity in the bond. The same interatomic distance of about 1.4 A may, however, correspond either to a double or to a single bond.

3. In order that all the available experimental material on interatomic distances in organic molecules may be in agreement with Butlerov's theory of structure, it is necessary to make the assumption, which has been suggested previously on several occasions, of the possibility of the existence in aromatic compounds not only of single and double bonds, but also of intermediate, "one-and-a-half fold" bonds, indicated in the schemes that follow by the sign λ. We shall not consider the nature of this bond in this paper. The object of our work here is quite different: we shall try to show the mutual effect of atoms and the possibility of representing any molecule by a single structural formula. The latter, of course, is possible only when there are experimental data of sufficient accuracy regarding the interatomic distances. For the representation of structural formulas of aromatic compounds, it is sufficient to use bonds of three types: single, double, and 1.5 - fold. Other things being equal, atoms bound by a distance intermediate between the distances appropriate for a single and for a double bond.

Kekulé's hypothesis contemplated the existence in aromatic compounds of carbon atoms of only one type $>C=$; we shall call this type A. The hypothesis stated above contemplates the existence of atoms not only of Type A, but also of a second type $>C-$; we shall call this Type B. In checking these ideas against the experimental material, we shall take the idea of the preservation of a definite symmetry in the molecules as our basis.

In studying the symmetry of large ions and of molecules of complex compounds, we concluded that in entering into the crystal such polyatomic structural units lose their symmetry according to a definite succession: high-order axes are lost most readily of all, then the planes, and finally the center, of symmetry [3]. If there is a center of symmetry in a complex ion or molecule, then it is generally preserved when the ion or molecule enters a crystal. This rule must hold all the more for organic compounds, for intermolecular forces (which are the main cause of the loss in symmetry of molecules on entering into crystals) are considerably weaker in organic than in inorganic compounds.

4. Let us examine the structure of the naphthalene molecule on the basis of the above discussion. Two "equivalent" structural formulas (I and II), having different dispositions of the double bonds, are given in textbooks for naphthalene (Fig. 3). The interatomic distances and the presence of a center of symmetry in the naphthalene molecule (III) [4] definitely indicates the superiority of structural formula II over I. The difference in distances between carbon atoms linked with like bonds . . . . $C = C$ . . . . . $= 1.37$ A ± 0.02 and . . . $C - C$ . . $= 1.41$ A ± 0.02 lies almost within the limits of experimental error. The central double bond is somewhat longer than the average double bond, and the outer single bonds are somewhat shorter than usual. This is what determines their equality in length.

The structure of the 1,5-dichloronaphthalene (IV, Fig. 3, Khaigorodsky and Kobalkina [5]) confirms, even better than the structure of the naphthalene molecule, the same localization of double bonds.

Fig. 3.

Unsurmountable difficulties are met in attempts to determine the disposition of double bonds in the anthracene molecule. If Kekule's formula for benzene is used, neither of the variants I and II (Fig. 4) can be reconciled with the existence of a center of symmetry in the anthracene molecule (II), which is definitely shown to exist by the X-ray investigations of Sinclair, Robertson, and Mathieson [6]. The same data, however, are in good agreement with the structural formula IV, constructed of carbon atoms of Type B. The distances between atoms linked by 1.5 fold bonds are each 1.39 ± 0.03 A. Replacement in the 1 5-positions of hydrogen by chlorine preserves the center of symmetry of the molecule (V), but leads to a rearrangement of bonds (VI) [5]. The increase in the two C—C distances (V) to 1.45 A in the central hexagon is associated with the repulsion of these hydrogen atoms from the chlorine atoms.

A different regrouping of bonds in the anthracene molecule is to be observed when oxygen is introduced in the 9- and 10-positions. The interatomic distances (according to Sen [7] in the anthraquinone molecule are shown in Fig. 4 (VII). The distribution of bonds is shown in formula VIII. The oxygen atoms are here bound by double bonds. The distance . . . . . . C=O . . . is 1.15 A. In carboxyl groups, however, the bonds between oxygen and carbon are identical ([2], see Fig. 2) and are evidently 1.5 fold, which should be indicated in the formula by the corresponding sign. The distance ...C—O is 1.25 A. In a single bond the ..C—O.. distance rises to 1.4 A or higher.

Returning to the structure of anthracene and its derivatives, we may note that, according to the type and position of a substituent, the numbers of carbon atoms of Type A and Type B may change considerably. Thus in anthracene all the carbon atoms are of Type B (Fig. 4). In 1,5-dichloroanthracene 8 carbon atoms are of Type A and 6 atoms are of Type B. In anthraquinone 12 carbon atoms are of Type B, and only 2 of Type A. For this
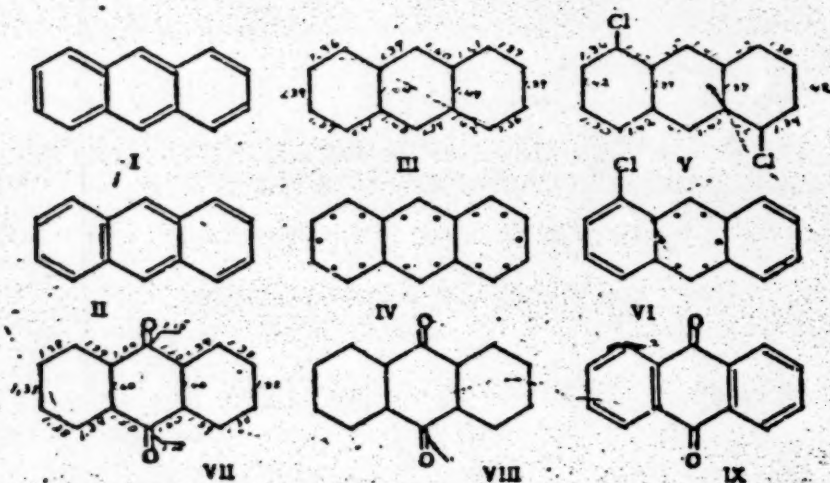

Fig. 4

molecule one might propose a Kekule bond distribution (IX), thus making it agree with the pseudosymmetry of the molecule VII. Such a distribution of bonds, however, would be very much at variance with the interatomic distances. It follows from our discussion that there is no strictly constant localization of double bonds in the benzene rings of aromatic compounds. Under the influence of different substituents the valency electrons may be rearranged, leading to a different localization of π-bonds, or to their complete delocalization in individual benzene rings (VI – VIII) or throughout the molecule (IV).

5. As a final example let us examine the structure of tropolone (Fig. 5). Compounds of this type are characterized by being much nearer in certain properties to aromatic than to aliphatic compounds. The results of the X-ray analysis of the Cu derivative of tropolone [6] permit us to understand the nature of this phenomenon. A study of the distances between the carbon atoms shows that there is an alternation of shorter and longer bonds in six sides of the ring (see the distances between carbon atoms 1,7, 7,6, 6,5, 5,4 and 4,3), which evidently permits us to assign double character to the shorter bonds. The seventh distance, 3,2, is again short. What is the multiplicity of this bond? The assigning of a multiplicity of two would be tantamount to the ascribing of quinquevalence to 3-C, and this, therefore, is impossible. This must therefore be a greatly shortened single bond. What is there to confirm this? If the 3,2 bond is a single one, then the 2-oxygen is linked to 2-C by a double bond. If the bond 2-C—O is

Fig. 5.

double, the bond 1-C—O is single. A comparison of the 1-C—O distance (1.34 A) with the 2-C—O distance (1.25 A) confirms such a distribution of double bonds in the molecule. The Cu—O distances also support such a distribution: 1-O has a free valency, and its distance from the copper atom is less than that of 2-O. On the other hand, the strongly electronegative oxygen (2-O) standing at a short distance from the ring of carbons attracts the hydrogen atom of the 3-CH g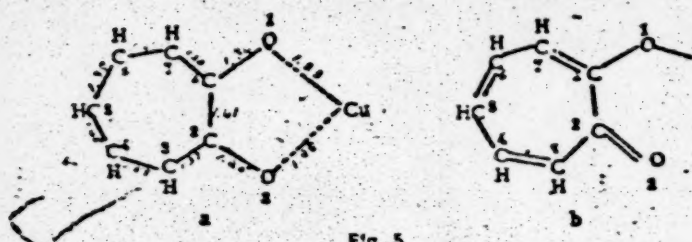roup, thus producing a considerable shortening in the 2,3-bond and conferring benzenoid properties on the whole ring. Such is the manner in which the mutual effects of atoms are manifested in this molecule.

Apart from this distribution of bonds (Fig. 5b), a second possible variant might be proposed, in favor of which may be cited the 2-C—O distance of 1.25 A, characteristic for a 1,5-fold bond, and also the exceptionally short 2,3-bond, which is shorter than any other C—C bond in the molecule. In this case we are bound to characterize the 2,3-bond as 1,5-fold, and the hydrogen, which participates in a hydrogen bond, we must consider as bound to neighboring atoms (3-C and 2-O) by single-electron bonds (C · H · O). The equivocality of the determination of the structural formula in this example does not involve a matter of principle. It is a consequence of the inadequate accuracy of the determination of the coordinates of hydrogen atoms in the crystal structure. An unequivocal answer regarding structural formulas can now be obtained in those cases in which they can be derived from the interatomic distances for atoms other than hydrogen atoms, mainly between carbon atoms. Unfortunately, the present level of X-ray analysis does not permit us to determine the positions of hydrogen atoms. For these purposes more hopeful methods are those of electronography and, particularly, neutronography. For the more restricted objects of this paper the equivocality of the determination of the structural formula of tropolone is not of great significance; what is more important is the fact that both of these possible solutions lead to the same conclusion, namely, that the "benzenoid" properties of the tropolone molecule are the result of the effect of the 2-oxygen atom on the interatomic distances. There are as yet no X-ray investigations that could supply data adequate for a consideration of the more general question of the resemblance or even identity in properties of substances having alternating double and single bonds with those having only 1,5-fold bonds; there are, however, also no obstacles in principle to the solution of these questions experimentally.

6. In conclusion we shall enumerate: 1) the assumptions that form the basis of this work; 2) the conclusions reached from an examination of the experimental material; and finally, 3) desirable further work, the performance of which could assist in the development of the ideas that have been put forward.

1) a In all compounds under examination carbon is quadrivalent, i.e., every carbon atom has 4 valency electrons. It is essential to begin with this supposition, for in a number of investigations this fact is forgotten and so not taken into account in the representation of structural formulas. Thus, according to Kitaigorodsky and Kobalkina [5] every carbon in naphthalene has on the average a valency of 4.6, and in anthracene a valency of 4.4.

b. The chemical bond between atoms in a molecule is effected by valency electrons, and a whole number of electrons participate in every bond.

c. The distance between carbon (and other) atoms, other things being equal, is the less, the greater the number of electrons participating in the formation of the bond.

2) **a.** The value of an interatomic distance for a given number of electrons participating in the bond may vary within fairly wide limits; thus, as a result of the mutual influence of atoms, certain bonds formed by a small number of electrons may be shorter than others formed by a greater number of electrons.

b. For the description of certain aromatic compounds having condensed benzene nuclei, the use of only single and double bonds or of only 1.5 fold (benzene) bonds is inadequate; it is necessary to consider all three types of bonds. It follows from this that every type of bond is defined by a whole number of electrons, though not necessarily an even number.

c. For every molecule it is possible to establish unequivocally, the structural formula so long as the dimensions of the molecule (the interatomic distances within it) and its symmetry have been determined with sufficient accuracy and the mutual influences of atoms have been taken into account (effect of individual atoms or groups on bond lengths).

d. Every compound is characterized by one single structure which can be described by one single structural formula with indications of the interatomic distances. This conclusion confirms the full correctness of the Butlerov-Markovnikov theory of structure, and it reveals the invalidity of the idea of representing a molecule by two or more structural formulas.

3) **a.** It would be of definite interest to investigate the chemical properties of bonds equal in multiplicity but greatly differing in length and equal in length but differing in multiplicity.

b. The correlation of the structural formulas obtained with physical and chemical properties of the compounds would also be of great interest.

In order not to increase the size of the paper we have confined ourselves to these few examples; we must point out however, that in all cases for which we were able to obtain the relevant literature the agreement of the hypotheses advanced above with the experimental data was not inferior to that found for our selected examples of aromatic compounds having condensed benzene rings. We may therefore conclude that the determination of the dimensions and symmetry of molecules is a rational method for the elucidation of the structures of organic compounds and of their representation by structural formulas and for the estimation of the mutual effects of atoms.

SUMMARY

1. It has been shown that the application of recent experimental data on interatomic distances in organic molecules makes it possible to characterize any given compound by one single structural formula.

2. It has been pointed out that the mutual effects of atoms may substantially change interatomic distances in molecules, and it is therefore necessary to take these effects into account when determining the structural formula.

3. It has been shown that for the representation of structural formulas that are compatible with the symmetry of the molecule, it is necessary in aromatic compounds having condensed benzene nuclei to take into account not only single and double bonds, but also intermediate, "1.5-fold" bonds.

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EFFECT OF THE PRESSURE APPLIED IN THE COMPRESSION OF AN
ALUMINA-MOLYBDENUM OXIDE CATALYST ON ITS ACTIVITY AND STRUCTURE

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In 1931 Plotnikov, Ivanov, and Pospekhov [1] showed that in the synthesis of methanol from carbon monoxide and hydrogen the activity of a ternary catalyst $Cu-ZnO-Cr_2O_3$ compressed at 300 atm was the same as that of an uncompressed catalyst of the same composition. A number of other investigators have found that at higher compression pressures there is a change in the specific activity and productivity of catalysts.* Thus, in an investigation of the decomposition reactions of methanol and ethanol on a compressed catalyst (zinc oxide) it was found [2] that increase in the compression pressure up to 5000 atm resulted in an increase in the productivity of the catalyst and a reduction in its specific activity. In more recent work [3] on the hydrogenation of mineral oils under a pressure of hydrogen in presence of compressed (up to 5000 atm) catalysts consisting of WS_2, NiS, and Al_2O_3 it was found that increase in the pressure applied in the compression of the catalysts had no significant effect on their specific activities, but somewhat increased their productivities.

Kurin and Perminov [4] made a detailed investigation of the decomposition of methanol at 275-375° in presence of a compressed zinc-chrome catalyst. According to their results, there is an appreciable rise in specific activity and productivity when the pressure at which the catalyst is compressed is increased to 5000 atm.; further increase in pressure to 10,000 atm leads to a reduction in the specific activity and productivity of the catalyst. The increase in activity of compressed catalysts was observed also by Ivannikov [5], who used a three-component catalyst $CaO-Al_2O_3-LiO_2$ compressed at 20,000 atm for the esterification of ethanol in absence of acid. The activity of this catlyst was found to be greater than that of uncompressed catslyst of the same composition.

Vereshchagin, Freidlin, Rubinshtein and Numanov [6] recently showed that, in the case of the dehydration of ethanol, aluminum oxide catalyst compressed at 20,000 atm. is more effective (productive), stable, and strong than catalysts that have not been subjected to compression. Also, the authors found that the compression caused no phase change in the aluminum oxide and that structural changes in the catalyst were associated with diminution in its macroporosity.

In the cases that have been investigated, therefore, compressed catalysts were found not only to be mechanically stronger, but also to have higher productivity in comparison with uncompressed catalysts. In the majority of the investigations cited (the exceptions being [2] and [4]) no study was made of the effect of the value of the compression pressure on the catalytic properties of the catalyst. In the present work we have investigated the effect of the value of the compression pressure (over the range 2000-20,000 atm.) on the structure of an alumina-molybdenum oxide catalyst and on its catalytic properties (productivity, specific activity, stability) in the reactions of dehydrocyclization of heptane and dehydrogenation of cyclohexane.

EXPERIMENTAL

Catalysts. An alumina-molybdenum oxide catalyst containing 20% by weight of MoO_3 was heated in a stream of hydrogen at 350° for 3 hours and at 500° for 2 hours. The catalyst, reduced in this way, was ground to a powder and subjected to pressure in lead ampoules under an all-direction hydrostatic pressure of 2000 atm. Part of the compressed catalyst so obtained was then further compressed under an all-direction hydrostatic pressure of 6000, 12,000, or 20,000 atm in lead ampoules in a superhigh-pressure multiplier. Compressed catalyst in grains 1.5-3 mm in diameter was required for the investigation. The charges, due to changes in compression pressure, in the "bulk" specific gravity of the granular catalysts obtained are given in Table 1. It follows from the data of Table 1 that the bulk specific gravity rises by 55% with increase in

* In this paper, the specific activity of a catlyst is its activity per unit weight, and its productivity is its activity per unit volume.

compression pressure from 2000 to 20,000 atm.

Catalyst No.	Compression pressure (atm)	Bulk specific gravity (g/cm³)
1	2000	0.78
2	6000	0.79
3	12000	1.00
4	20000	1.20

Apparatus, Procedure, and Method of Investigating Catalysts. The experiments were carried out without the use of a gas-carrier, the flow method being employed. The pressure was atmospheric in the catalysis tube (length 1100 mm, internal diameter 7 mm), which was made of Pyrex glass and was mounted on an inclined catalysis furnace provided with electric heating and temperature regulation. In all experiments on the determination of the activity of the catalysts, the temperature was maintained in the range 489–491°.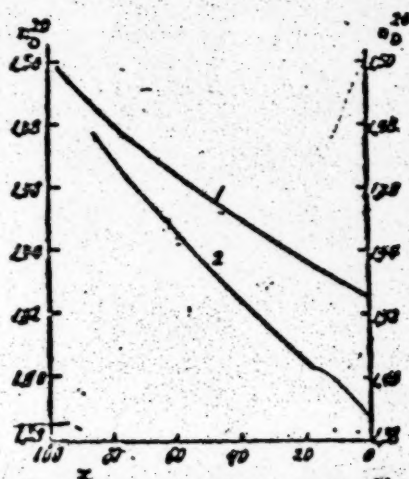 A layer of catalyst 16.5 cm long was placed in the catalysis tube. All experiments were carried out with 6 cm³ of catalyst (always measured in the same glass cylinder). In the main experiments the duration was 4 hours, but in those on productivity it was 2–4 hours. In the experiments, regenerated catalysts of stable activity were always used. In order to stabilize their activities, fresh portions of catalyst were heated in a stream of hydrogen for 2 hours at 500°, after which a 2-hour experiment with heptane at 489–491° was carried out. The catalyst was then regenerated (this was done also after other experiments under the same conditions): the catalyst was blown with nitrogen for 30 minutes, then with air at 500° for about one hour, after which air was displaced by nitrogen and the catalyst was reduced with hydrogen at 500° for 1-2 hours. When these operating conditions were observed with the catalyst, the experiments were found to be sufficiently reproducible.

Hydrocarbons having the following constants were used: heptane — b.p. 98.2 - 98.3° at 760 mm; d_4^{20} 0.6838; n_D^{23} 1.3876 (literature [8] gives: b.p. 98.4° at 760 mm; d_4^{20} 0.6837, n_D^{20} 1.3876); cyclohexane — b.p. 80.7 - 80.6° at 760 mm; d_4^{20} 0.7765; n_D^{23} 1.4265 (literature [8] gives: b.p. 80.7° at 760 mm; d_4^{20} 0.7766; n_D^{20} 1.4262).

During the experiments the hydrocarbons were passed to the catalysis tube always at the same space velocity of 0.55 ml of hydrocarbon per 1 cm³ of catalyst per hour; this was carried out with the aid of a piston device for delivering liquids at a constant rate [7]. The device was operated by means of a small CD-2 motor. The catalyzate passed from the reaction tube to a receiver cooled by a mixture of ice and water and connected to a trap cooled to −70°. In order to remove the small amount of catalyzate that was generally held back at the end of the catalysis tube, the latter was provided with a special drain made from aluminium foil. The weight of the liquid that collected in the trap during the experiment was divided by the number of hours that had passed, and the result was added to the weight of catalyzate obtained per hour in the given experiment. At the end of each experiment, starting substances adsorbed by the catalyst and reaction products were displaced by nitrogen and their weight determined so that it might be added to the weight of catalyzate obtained in the first hour of the experiment.

In the course of the experiments catalyzates were collected separately every hour, and their refractive indices and yields (g) were determined. At the end of the experiment all the

Fig. 1. Dependence of the refractive index n_D^{20} of catalyzate on its content of aromatic hydrocarbons: 1) Cyclohexane catalyzates; 2) heptane catalyzates (x is the concentration of aromatic hydrocarbons in the catalyzate in % by weight).

* The bulk specific gravity was determined by weighing 6 cc of catalyst (in grains of diameter 1.5-0mm) measured in a particular glass cylinder having a capacity of 10 ml.

catalyzates collected were united, and the refractive index of the catalyzate obtained over the whole course of the experiment was determined. For the determination of the degree of conversion of heptane or cyclohexane into aromatic hydrocarbons, we made use of curves relating the refractive indices of the catalyzates from these hydrocarbons to their contents of aromatic hydrocarbons. The relevant curves, which are given in Fig. 1, were constructed on the basis of investigations of 60 catalyzates from heptane and 54 catalyzates from cyclohexane, which were obtained in the presence of alumina-molybdenum oxide catalysts at 450-500°, the concentration of aromatic hydrocarbons being determined by the method of relative dispersion proposed by Ioffe [9, 10]. The curves given cover data on the refractive indices of catalysts containing from 6 to 97% of aromatic hydrocarbons.

TABLE 2

Activity of Compressed Catalysts in the Dehydrocyclization of Heptane*

Expt. No.	Catalyst No.	Compression pressure (atm)	Time (hr)	Amt. of hydrocarbons passed (ml)	Yield of catalyzate (% by wt.)	n_D^{18} of catalyzate	Content of aromatic hydrocarbons in catalyzate (% by wt.)	Productivity of catalyzate	Specific activity of catalyzate
126	1	2000	0-1	3.50	67.8	1.4182	33.9	3.83	4.91
			1-2	3.50	79.9	1.4076	22.3	2.97	3.81
			2-3	3.55	86.9	1.4028	16.5	2.45	3.13
			3-4	3.55	88.5	1.4001	12.1	1.78	2.29
		Total Mean		14.10	81.3	1.4057	20.5	2.78	3.56
121	2	6000	0-1	3.55	58.0	1.4214	37.0	3.58	4.56
			1-2	3.60	83.3	1.4082	23.1	3.20	4.08
			2-3	3.50	85.8	1.4035	17.5	2.50	3.19
			3-4	3.60	88.2	1.4003	12.8	1.88	2.40
		Total Mean		14.25	78.9	1.4063	21.0	2.77	3.52
116	3	1200	0-1	3.50	64.4	1.4236	39.0	4.22	4.17
			1-2	3.60	85.4	1.4080	22.5	3.20	3.19
			2-3	3.50	85.4	1.4026	16.5	2.35	2.35
			3-4	3.60	87.0	1.4008	13.7	1.98	1.98
		Total Mean		14.20	80.6	1.4070	21.8	2.93	2.93
132	4	20000	0-1	3.50	60.7	1.4245	39.9	4.04	3.36
			1-2	3.60	75.6	1.4134	28.5	3.58	2.98
			2-3	3.50	88.3	1.4066	21.1	3.10	2.58
			3-4	3.55	86.4	1.4028	16.8	2.42	2.01
		Total Mean		14.15	77.8	1.4093	24.1	3.13	2.61

Results of the Investigation of the Activity of Compressed Catalysts. As indicated above, the object of this work was the elucidation of the effect of the value of the pressure applied in the compression of catalysts on their catalytic properties. In Tables 2 and 3 results are given that characterize the effect of the pressure applied in the compression of catalysts on their activity in the reactions of dehydrocyclization of heptane

* Space rate 0.59; temperature of experiments 489-491°, volume of catalyst 6 cm³.

and dehydrogenation of cyclohexane. We determined the activity in the form of the degree of conversion (in % by wt.) of the original hydrocarbons into aromatics referred to 1 cm³ of catalyst (productivity) or to 1 g of catalyst (specific activity) at constant space rate (0.59 ml of hydrocarbon per 1 cm³ of catalyst per hour).

TABLE 3
Activity of Compressed Catalysts in the Dehydrogenation of Cyclohexane *

Expt. No.	Catalyst No.	Compression pressure (atm)	Time (hr)	Amt. of hydrocarbons passed (ml)	Yield of catalyzate (% by wt.)	n_D^{18} of catalyzate	Content of aromatic hydrocarbons in catalyzate (% by wt.)	Productivity of catalyzate	Specific activity of catalyzate
128	1	2000	0-1	3.60	71.4	1.4683	65.0	7.73	9.92
			1-2	3.50	82.7	1.4566	49.8	6.86	8.80
			2-3	3.50	88.6	1.4513	41.9	6.18	7.93
			3-4	3.55	89.1	1.4464	34.2	5.08	6.51
			Total	14.15					
			Mean		82.9	1.4541	46.0	6.35	8.15
124	2	6000	0-1	3.50	72.1	1.4671	63.9	7.68	9.78
			1-2	3.50	85.3	1.4564	49.5	7.03	8.96
			2-3	3.55	89.5	1.4497	39.8	5.93	7.56
			3-4	3.50	90.8	1.4454	32.9	4.98	6.34
			Total	14.05					
			Mean		84.4	1.4525	43.9	6.18	7.88
119	3	12000	0-1	3.50	67.1	1.4717	69.0	7.71	7.70
			1-2	3.50	83.5	1.4624	57.4	7.98	7.97
			2-3	3.55	87.0	1.4558	48.3	7.00	6.99
			3-4	3.50	86.4	1.4517	42.2	6.08	6.07
			Total	14.15					
			Mean		80.9	1.4567	52.5	7.09	7.07
136	4	20000	0-1	3.50	78.3	1.4703	67.8	8.86	7.36
			1-2	3.50	84.2	1.4578	51.0	7.15	5.95
			2-3	3.60	85.7	1.4561	48.9	6.99	5.81
			3-4	3.50	88.2	1.4533	44.5	6.53	5.44
			Total	14.10					
			Mean		84.1	1.4582	51.7	7.25	6.03

Examination of the results in Tables 2 and 3 permits us to conclude that increase in the pressure applied in the compression of an alumina–molybdenum oxide catalyst leads to a rise in its productivity. At the same time, the results indicate a reduction in the specific activity of compressed catalysts, in the reactions we have investigated, as the pressure applied for their compression is increased.

Results of X-ray Investigations of Catalysts. Investigations were carried out on samples of catalysts that had been reduced but not yet used for the aromatization of the hydrocarbons. Photographs were taken on Kodak film in a Debye camera, having a film holder 57 mm in diameter, by means of the series K_α rays of iron (λ = 1.932A), the exposure being 10 hours at 12 mA and 30 kV.

* Space rate 0.59, temperature of experiments 469-491°; volume of catalyst 6 cm³.

Fig. 2. X-Ray diffraction photographs.

1) Uncompressed catalyst;

2) Catalyst No. 1.

3) Catalyst No. 3.

The X-ray photographs of the original catalyst and of samples compressed at pressures of 2000 and 12,000 atm are given in Fig. 2 (see page 29). The identical positions of the lines and the identical widths of corresponding lines on all of the X-ray photographs indicate that, firstly, compression at pressures of up to 12,000 atm does not result in any change in the phase composition of the mixed catalyst under investigation, and, secondly, the dimensions of the elementary crystals (i.e., the degree of dispersion) are not affected over this range of pressures.

TABLE 4
Results of the X-Ray Analysis of Alumina—Molybdenum Oxide Catalysts

Uncompressed sample		Catalyst No. 1 (compressed at 2,000 atm)		Catalyst No. 3 (compressed at 12,000 atm)	
d (A)	Intensity	d (A)	Intensity	d (A)	Intensity
2.24	medium	2.24	medium	2.24	medium
2.09	v. weak	2.05	v. weak	2.07	v. weak
1.88	strong	1.87	strong	1.89	strong
1.63	v. weak	—		1.65	v. weak
1.47	medium	1.47	medium	—	
1.35	v. strong	1.34	v. strong	1.36	v. strong
1.17	weak	—		—	
1.13	weak	1.12	weak	1.12	weak

The X-ray results in Table 4 show that the values of the interplanar distances (d) for catalysts Nos. 1 and 3 have changed to such an insignificant extent from those for the uncompressed catalyst that the observed variations could be assigned entirely to experimental error. Exceptions are found in the values of d for the very weak lines, the exact measurement of which is difficult. The results in Table 4 show also that the crystalline phase in the investigated samples is γ-

Al_2O_3 having a somewhat deformed lattice, evidently owing to the dissolution in it of part of the MoO_2 present in the catalyst. As the catalysts have the characteristic color of MoO_2, it must be considered that an appreciable part of it is present as an independent phase, in spite of the absence of MoO_2 lines in the X-ray photographs. This view is confirmed by results for the values of the parameter of the crystal lattice of γ-Al_2O_3 and the deformation of the lattice; these are given in Table 5.

TABLE 5
Deformation of the Crystal Lattice of γ-Al_2O_3 in the Samples Investigated

Sample	a (A)	Deformation relative to uncompressed sample (%)	Deformation relative to value of a from tables	
			(%)	(A)
Uncompressed	7.75	—	−2.0	0.16
Catalyst No. 1 (compressed at 2000 atm)	7.72	−0.37	−2.4	0.19
Catalyst No. 3 (compressed at 12,000 atm)	7.74	−0.14	−2.2	0.17
Value from tables	7.91			

Thus, already in its original condition the catalyst contains γ-Al_2O_3 having a deformed lattice. Its mean compression amounting to 0.18 A or 2.2%. In view of the values of the parameters of the lattice of MoO_2 (c = 4.86A, a = 2.88A, rutile type), the observed change in the parameter of the lattice of γ-Al_2O_3 indicates the formation of a solid solution containing a low concentration of MoO_2. As the MoO_2 content of the catalyst is considerable (about 20%) and there are no corresponding reflec-

tions on the X-ray photographs, it must be concluded that the part of the MoO_2 that has not passed into the lattice of γ-Al_2O_3 is in a state that is amorphous to X-rays. The practically constant value of the lattice deformation of γ-Al_2O_3 at various pressures indicates that the compression did not affect the composition of the solid solution.

The general conclusion from the X-ray analysis of the samples of catalyst is as follows: compression at pressures of up to 12,000 atm does not cause any change in the phase composition and primary (X-ray) structure of the investigated catalyst. The observed changes in its physical properties (increase in bulk specific gravity, hardness, and strength) must be attributed to changes in secondary structure, in particular, porosity.

DISCUSSION OF RESULTS

The results obtained in this investigation have extended our information on the effect of the pressure

applied in the compression of catalysts on their activity. These results lead to the conclusion that the productivity of the compressed catalysts that we have investigated is determined by two quantities - the specific activity and the bulk specific gravity, which change in opposite directions as the compression pressure is increased.

It follows from an examination of Fig. 3, that increase in the compression pressure from 2000 to 20,000 atm leads to an increase in the productivity of the catalyst in both of the investigated reactions by 12-14%; under these conditions the specific activity falls by 26-27%. The absence of significant changes in the crystalline structure of the catalysts after their subjection to a hydrostatic pressure is evidence for the supposition that the observed fall in specific activity is associated with the change in the porosity of the catalyst.

Let us pass to an examination of the stability of compressed catalyst. Analysis of the results given in Tables 2 and 3 shows that reduction in the specific activity of the catalyst (c) with increase in the duration of the experiment τ may be expressed by a straight line on the graph of log c against τ (Fig. 4), i.e. by the equation:

$$\log c = \log c_0 - \alpha \tau.$$

Fig. 3. Effect of compression pressure on productivity (1) and specific activity (2) of alumina-molybdenum oxide catalysts. o—dehydrocyclization of heptane; •—dehydrogenation of cyclohexane.

In this equation c_0 is the specific activity of the catalyst at τ = 0; the value of the coefficient α characterizes the rate at which the specific activity of the catalyst falls in the course of use (instability of the catalyst). It is found desirable to characterize the stability of the catalyst by the coef-
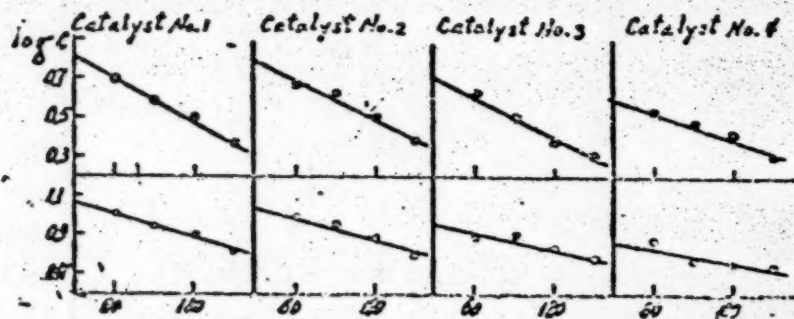
Fig. 4. Stability of compressed alumina-molybdenum oxide catalysts in the course of use: o—dehydrocyclization of heptane; •—dehydrogenation of cyclohexane (c is the specific activity of the catalyst).

ficient β, equal to 1/α. The value of the stability coefficient β increases with increase in the compression pressure (Table 6). We have as yet no basis, however, upon which to conclude that this increase in stability

is a specific effect of the high compression pressure. We cannot exclude the possibility that the observed increase in the stability of compressed catalysts is associated with their reduced specific activity, as has been observed in a number of cases for uncompressed catalysts. In order to solve this important question, further investigations are required.

In conclusion we may point out that the increase in the coefficient β is approximately the same for both of the investigated reactions (62-77 %).

TABLE 6

Effect of the Pressure Applied in the Compression of Catalysts on the Value of the Stability Coefficient β.

Pressure P (atm)	Dehydrogenation of cyclohexane		Dehydrocyclization of heptane	
	β (hr)	$\beta_p : \beta_{2000}$	β (hr)	$\beta_p : \beta_0$
2000	17.4	1.00	8.9	1.00
6000	18.2	1.05	10.2	1.15
12000	22.2	1.28	10.0	1.12
20000	30.7	1.77	14.8	1.67

SUMMARY

1. An investigation has been carried out into the effect of the value of the compression pressure (in the range 2000-20,000 atm) on the structure of compressed alumina—molybdenum oxide catalyst and on its productivity, specific activity, and stability in the reactions of dehydrocyclization of heptane and dehydrogenation of cyclohexane.

2. It has been shown that increase in compression pressure leads to increase in the productivity and decrease in the specific activity of the catalyst (to an equal extent for both of the investigated reactions).

3. It has been found that the stability of compressed alumina—molybdenum oxide catalyst increases with the compression pressure (also to an equal extent for both of the investigated reactions).

4. X-Ray investigation has not revealed any changes in the primary (X-ray) structure of the catalyst after it has been subjected to a high hydrostatic pressure.

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ADSORPTION OF GAS MIXTURES

COMMUNICATION 3. POSSIBILITY OF A STATISTICAL TREATMENT
OF THE ADSORPTION PHENOMENA OF GAS MIXTURES

B. P. Bering and V. V. Serpinsky

We shall consider that the fundamental problem in the theory of the adsorption of gas mixtures is the calculation of the adsorption of the components of the mixture for given values of the equilibrium partial pressures, the isotherms for the adsorption of the pure components being known at the same temperature. If we confine ourselves to the examination of the binary mixtures, this problem may be formulated as follows: It is required to calculate the values of the functions

$$a_1 = f_1(p_1, p_2) \text{ and } a_2 = f_2(p_1, p_2) \tag{1}$$

the functions $a_1^\circ = f_1(p_1, 0)$ and $a_2^\circ = f_2(0, p_2)$ being given (graphically or analytically); a_1 and a_2 are the adsorption values for the components of the mixture; a_1° and a_2° are the corresponding values for the adsorption of pure component; and p_1 and p_2 are the equilibrium partial pressures (here and elsewhere in this paper the gas phase is considered to be ideal).

In the solution of this problem we may start from different physical representations of the adsorption process. It may be assumed, of course, that any molecular—kinetic or thermodynamic theory of adsorption may be generalized to the case of the adsorption of a mixture. This generalization may sometimes be performed without the introduction of any new constants, i.e., all the constants necessary for the description of the adsorption of a mixture may be obtained by the investigation of the adsorption of the pure components. It is obvious that in this case the solution of the problem stated above is possible. Such a case is found in the well known simple theory of Langmuir adsorption. In certain cases a similar generalization is in principle impossible without the introduction of some new constants. Magnus' theory [1] is one of this type. It will be clear that in these cases the functions $a_1^\circ = f_1(p_1, 0)$ and $a_2^\circ = f_2(0, p_2)$ are insufficient for the calculation of the functions expressed by Equations 1.

In this paper we shall confine ourselves to the examination of certain aspects of the theory of adsorption of binary gas mixtures, the postulate being made that in the system under investigation all prerequisites demanded by Langmuir's theory are realized with the exception of the assumption of energetic homogeneity over the surface. As is well known, Langmuir himself pointed out that for surfaces having adsorption sites of several types it is possible to apply the concepts relating to a homogeneous surface to each assembly of identical sites and to calculated the adsorption over the whole surface by summation of the adsorption values for all the assemblies. This demonstration, however, remained in the form of a schematic formula, for there were no methods available for the practical performance of such a calculation. Substantial progress in this direction was made by Zeldovich [2] who, in the place of a discreet set of energies of adsorption, introduced a continuous function for the surface distribution according to adsorption energy values (or adsorption coefficient values) and found an analytical expression for the adsorption isotherm for a definite form of this distribution function. This line of work, mainly as a result of Roginsky's investigations, developed into an orderly theory of adsorption and catalytic phenomena on heterogeneous surfaces. A detailed exposition of the theory and its numerous applications, and also a history of the question, are given by Roginsky in his monograph [3].

It must be pointed out that Roginsky and Todes [4] have extended this theory to the case of the adsorption of gas mixtures and, with the aid of certain supplementary assumptions, have solved the problem formulated at the beginning of this paper. In a later part of this paper we shall compare the results obtained by Roginsky and Todes with the results of the analysis of the problem that now follows.

Let us assume that the surface may be characterized by a distribution function $\rho(b_1, b_2)$ in terms of two adsorption coefficients b_1 and b_2, which may in general be regarded as independent variables. It is evident that

$$\int_0^\infty \int_0^\infty \rho(b_1, b_2)\, db_1\, db_2 = 1 \tag{2}$$

In the case of adsorption from a mixture, the degree of filling of the surface by, for example, the first component will be expressed in its most general form, with all the assumptions already made, by the following equation:

$$\theta_1 = \int_0^\infty \int_0^\infty \frac{b_1 p_1}{1 + \sum b_i p_i} \rho(b_1, b_2)\, db_1\, db_2. \tag{3}$$

From the very beginning we shall confine ourselves to a consideration of the case in which b_2 is a single-valued function of b_1. On the basis of very general considerations, it may be concluded that this case is always realized in physical adsorption. If $b_2 = \varphi(b_1)$, then $\rho(b_1, b_2) = \rho[b_1, \varphi(b_1)] = \rho(b_1)$, and for the calculation of the degree of filling a knowledge of the distribution function, e.g., with respect to b_1, is sufficient. Equation 3 may be simplified and written as follows:

$$\theta_1 = \int_0^\infty \frac{b_1 p_1}{1 + b_1 p_1 + b_2 p_2} \rho(b_1) db_1; \qquad \theta_2 = \int_0^\infty \frac{b_2 p_2}{1 + b_1 p_1 + b_2 p_2} \rho(b_1) db_1; \tag{4a}$$

$$\theta_{12} = \theta_1 + \theta_2 = \int_0^\infty \frac{b_1 p_1 + b_2 p_2}{1 + b_1 p_1 + b_2 p_2} \rho(b_1) db_1. \tag{4b}$$

It may be noted that for the sake of generality integration limits of zero and infinity have been indicated in Equations 4; it is in fact sufficient to integrate from a certain b_1 min to a certain b_1 max, since for values of b_1 higher than b_1 max and less than b_1 min, the function $\rho(b_1)$ becomes zero.

There is reason to suppose that in the most general case no further simplifications of Equations 4 are possible. The possibility of utilizing these equations practically is now determined by the possibility of the reliable determination of the function $\rho(b_1)$, from investigation of the adsorption of the pure component, and of the function $b_2 = \varphi(b_1)$, from some other considerations. Considerable interest is presented, however, by the examination of various special cases in which certain assumptions concerning the form of the functions $b_2 = \varphi(b_1)$ or $\rho(b_1)$ permit us to proceed very much further instead of confining ourselves to the simple writing out of Equations 4.

It may be noted further that for the complete description of the adsorption equilibrium in the case of a gas mixture, it is possible to calculate, instead of the quantities a_1 and a_2 (or θ_1 and θ_2), the values of the total adsorption $a_{12} = a_1 + a_2$ (or $\theta_{12} = \theta_1 + \theta_2$) and of the so-called selectivity coefficient α_2 [5], defined by the equation:

$$\alpha_2 = \frac{N_2^\sigma N_1}{N_1^\sigma N_2} = \frac{a_2 p_1}{a_1 p_2} = \frac{\theta_2 p_1}{\theta_1 p_2} \tag{5}$$

(here N_2^σ and $N_1^\sigma = 1 - N_2^\sigma$ are the molar fractions of the components in the adsorbed phase, and N_2 and $N_1 = 1 - N_2$ are the corresponding quantities for the equilibrium gas phase). It is clear that a knowledge of the values of a_{12} and α_2 for given values of the independent variables p_1 and p_2 will permit us to calculate the corresponding values of a_1 and a_2.

The first case that we shall examine is a completely trivial one. For a homogeneous surface (as a special case of a heterogeneous one), Equations 4 may be clearly written in the form:

$$\theta_1 = \frac{b_1 p_1}{1 + b_1 p_1 + b_2 p_2}; \quad \theta_2 = \frac{b_2 p_2}{1 + b_1 p_1 + b_2 p_2}; \tag{6a}$$

$$\theta_{12} = \frac{b_1 p_1 + b_2 p_2}{1 + b_1 p_1 + b_2 p_2} \tag{6b}$$

It must be emphasized that in the expression $\theta_1 = \frac{a_1}{a^m}$ where a^m is the maximum adsorption in a monomolecular layer, the value of a^m is the same for each component. The alternative supposition is not compatible with the molecular-kinetic picture upon which the concept that we are discussing is based, and it leads to a thermodynamic contradiction. We have examined this question in detail [5].*

* After the publication of our paper [5] we learned of a paper which had previously escaped notice, by I. R. Krichevsky, (L. Phys. Chem., 5, 742, 1934), in which, long before our work and with exhaustive completeness and rigor, the incompatibility of the postulate $a^m \neq a^{mic}$ with the Gibbs-Duhem equation was proved.

From this point of view the well known work of Markham and Benton [6] on the adsorption of gas mixtures is not valid, since it is there assumed that $a_1^m \neq a_2^m$. For the same reason certain conclusions of Lewis and co-workers [7] are invalid; they also assume that $a_1^m \neq a_2^m$.

Since the coefficients b_1 and b_2 can readily be determined for a homogeneous surface from data on the absorption of the pure components, Equations 6 give a complete solution to this problem.

For our further considerations, the following remarks are of importance. If we plot equilibrium partial pressures p_1 and p_2 along two axes of coordinates (Fig. 1) and values of a_1, a_2, or a_{12} along the third axis, then it follows from Equations 6 that the projections of the summation isosteres of adsorption $a_{12} = $ const. on the plane $a_1 = 0$ form a family of parallel straight lines having slopes of $-b_1/b_2$; the projections of the adsorption isosteres of the first component of the mixture on the same plane form a family of straight lines, which, when continued, intersect at one point having the coordinates $(0, -1/b_2)$; the rectilinear isosteres for the second component, when continued, also intersect at one point, which has the coordinates $(-1/b_1, 0)$.

From Equations 6 it follows that the selectivity coefficient in the case of a homogeneous surface does not depend on p_1 and p_2 and is equal to the ratio of the coefficients b_2 and b_1:

$$\alpha_2 = \frac{b_2}{b_1}. \tag{7}$$

The second special case that we shall examine concerns a heterogeneous surface, and it may be formulated as follows. Let the difference in the energy of adsorption for a transition from adsorption sites of one type to those of another be the same for each component:

$$\epsilon_2 - \epsilon_1 = \text{const.} \tag{8}$$

Since

$$b_1 = b_{10} e^{\epsilon_1/RT} \tag{9}$$

(b_{10} is a certain constant, the physical significance of which we shall consider later), the condition of Equation 8 is equivalent to the condition:

$$\frac{b_2}{b_1} = \frac{b_{20}}{b_{10}} e^{(\epsilon_2-\epsilon_1)/RT} = k = \text{const.} \tag{10}$$

By the use of Equation 10 and an examination of the total adsorption isotherm

Figure 1.

($a_{12} = $ const.), we may rewrite Equation 4b in the form:

$$\theta_{12} = \frac{a_{12}}{a^m} \times \int_0^\infty \frac{p_1 + kp_2}{\frac{1}{b_1} + p_1 + kp_2} \rho(b_1)db_1 = \text{const.} \tag{11}$$

Equation 11 enables us to determine the form of the curve $p_2 = \varphi(p_1)$, along which a_{12} remains constant (in other words, enables us to determine the equation of the projection of the isostere for total adsorption on the plane $a_1 = 0$). It is clear that along this curve

$$\frac{1}{a^m} \frac{da_{12}}{dp_1} = \int_0^\infty \frac{\frac{1}{b_1}\left(1 + k\frac{dp_2}{dp_1}\right)}{\left(\frac{1}{b_1} + p_1 + kp_2\right)^2} \rho(b_1)db_1 = 0. \tag{12}$$

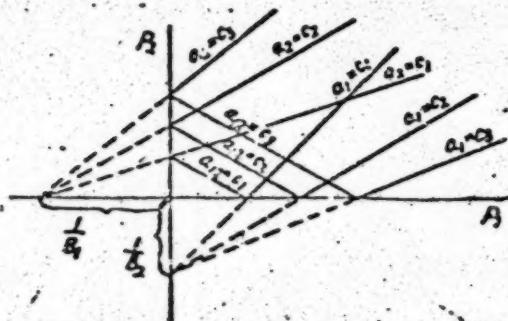Equation 12 is satisfied if

$$1 + k \frac{dp_2}{dp_1} = 0 \tag{13}$$

Equation 12 has no other solutions, for in accordance with the physical sense of the quantities involved in it, the function

$$\frac{\frac{1}{b_1} \rho(b_1)}{\left(\frac{1}{b_1} + p_1 + kp_2\right)^2}$$

is essentially positive.

It follows from Equation 13 that

$$p_2 = -\frac{1}{k} p_1 + C. \tag{14}$$

When the condition of Equation 8 is observed, therefore, irrespective of the form of the distribution function, the projections of the total adsorption isosteres on the plane $a_1 = 0$ are straight lines.*

In the second communication [8] of this series it was shown that, in all of the cases that we have examined of the adsorption of binary mixtures of gases, the projections of the total adsorption isosteres on the plane $a_1 = 0$ are indeed straight lines. It is, however, difficult, if not impossible, to imagine an adsorption mechanism for which the condition of Equation 8 would be realized. The question of the conditions under which Equation 14 can be fulfilled (exactly or approximately), apart from the case defined by Equation 8, is therefore of some interest.

Before making an analysis of this matter we will show how the selectivity coefficient α can be expressed when the condition of Equation 8 is observed. For each given type of adsorption sites the coefficient α is expressed by Equation 7. Since Equation 10 may be derived from Equation 8, in this case α remains constant for the whole surface (with the natural assumption that the coefficients b_{10} do not change on passing from one type of sites to another) and is given by

$$\alpha_2 = \frac{b_{12}}{b_{11}} e^{(\epsilon_2 - \epsilon_1)/RT} \tag{15}$$

The possibility of making an approximate calculation from Equation 15 will be discussed below.

An examination of possible adsorption mechanisms leads to the view that for physical adsorption the most probable form of relationship between ϵ_2 and ϵ_1 will be

$$\frac{\epsilon_2}{\epsilon_1} = \beta \tag{16}$$

where β is some constant, which, in the case of adsorption due to dispersion forces, for example, is equal to the first approximation to the ratio of the polarizabilities of the molecules of the two components. From Equations 16 and 9 we may write

$$\frac{b_2}{b_1} = \frac{b_{22}}{b_{18}} b_1^{\beta-1} = k' b_1^{\beta-1}. \tag{17}$$

where k' is a constant. Comparison of Equations 10 and 17 shows that when β is sufficiently close in value to unity (i.e. in the case when the adsorption energies of the two components are very close together in value) all the conclusions that can be rigorously drawn from Equation 10 are approximately true also when the condition in Equation 16 is observed, the closeness of the approximation being the greater, the lower the value of $\delta = \beta - 1$.

* In a discussion of the questions examined in this paper, S. Z. Roginsky pointed out to us that Equation 14 could be obtained from a comparison of the equation

$$\theta_2^0 = \int_0^\infty \frac{b_1 p}{1 + b_1 p} \rho(b_1) db_1$$

with Equation 4b, the additional postulate that $\theta_1^0 = \theta_{11}^0$ being made.

Thus, when the condition most frequently realized in practice, i.e. that expressed in Equation 16, is observed, and at sufficiently low values of δ, irrespective of the form of the distribution function, Equations 14 and 15 must be approximately correct. In the limit, when $\delta = 0$, the condition of Equation 16 becomes equivalent to that of Equation 8, and Equations 14 and 15 become strictly accurate.

It is easy to show that the second limiting case, when the components of the mixture differ greatly in their adsorption energies (more exactly, when $\epsilon_2 - \epsilon_1 \gg RT$, which is practically equivalent to the condition that β must be a quantity of the order of unity or greater), corresponds to the solution given by Roginsky and Todes [4] (with the supplementary condition that $\epsilon_{1\ max} - \epsilon_{2\ min} \gg 4RT$). As these authors do not make sufficiently clear that their solution is valid only under the condition that $\epsilon_2 - \epsilon_1 \gg RT$ *, we considered it desirable to discuss this matter briefly. We shall confine ourselves to an analysis of only two of the conclusions that Roginsky and Todes reach.

The ratio of the degrees of filling of a given type of adsorption site by the two components is calculated by Roginsky and Todes from a formula that has the following form in our notation:

$$\frac{\theta_2}{\theta_1} = \frac{b_{2s}}{b_{1s}} \frac{p_2}{p_1} e^{\epsilon_1(\beta - 1)/RT}. \tag{18}$$

If p_1 and p_2 are of the same order (and all the more if $p_2 \gg p_1$), Roginsky and Todes consider that for all types of sites the value of θ_1 may be neglected in comparison with θ_2. It is clear that this conclusion is valid only if $\epsilon_1(\beta - 1) \gg RT$. For sufficiently high values of p_2, $\theta_2.\theta$ may attain the value of unity (for a definite value of $\epsilon_1 = \epsilon_1^*$) From Equation 18 we obtain

$$\epsilon_1^* = \frac{RT}{\beta - 1} \ln \frac{p_2 b_{2s}}{p_1 b_{1s}}. \tag{19}$$

Roginsky and Todes consider that when $\epsilon_1 > \epsilon_1^*$, then θ_1 may be neglected in comparison with θ_2, and when $\epsilon_1 < \epsilon_1^*$, then θ_2 may be neglected in comparison with θ_1. It is quite obvious that this conclusion is valid only when $\epsilon_1(\beta - 1) \gg RT$, and this condition is practically equivalent to the condition $\beta \gg 1$.

It should be pointed out that among the cases considered by Roginsky and Todes there is one for which the condition $\beta \gg 1$ is not required. This is the case when there is no correlation between the adsorption energies of the separate components. It was for this case, however, that these authors did not find it possible to exclude the distribution coefficient from the expressions for the adsorption of the mixture.
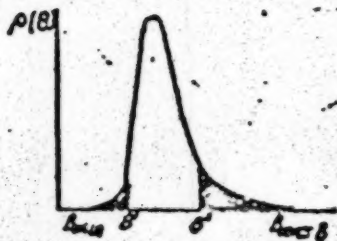

Fig. 2.

Let us return again to the analysis of Equations 4. It may be considered that in the investigation of physical adsorption the most interesting case from the practical point of view occurs when the condition in Equation 16 is observed and the value of β, although close to unity, is not so close that Equation 10 may be considered a good approximation to Equation 17. In this case, a fairly good approximate solution of the problem is possible if a certain limitation (in our opinion, a quite natural limitation) is placed on the form of the distribution function. We shall consider that the distribution function has a fairly sharp maximum. Physically, this means that, although types of sites associated with widely differing adsorption energies (and therefore adsorption coefficients) are to be found on the surface, the proportion of such sites is comparatively low. In other words, the integration in Equations 4 may be carried out, to a good approximation, by using as limits not b_{min} and b_{max}, but the considerably narrower limits b' and b'' (Fig. 2), b' and b'' being such that outside them the distribution function has values not far removed from zero. It is clear that this method of integration implies the neglecting of

* The condition $\epsilon_{1\ max} - \epsilon_{1\ min} \gg 4RT$ is expressed quite clearly by these authors.

the area shaded in Fig. 2 in comparison with the whole area under the curve. It is obvious that the positions of b' and b'' cannot be fixed exactly; they are determined by the form of the distribution curve and the desired degree of accuracy. It is clear also that such a method of integration is inapplicable for very low degrees of filling, for which the rejected types of sites may play a decisive part.

Let us determine by what factor the ratio b_2/b_1 may change in the chosen range from b' to b''. From Equations 17 and 9 we may write

$$\frac{b_2'}{b_2''} : \frac{b_1'}{b_1''} = e^{(\epsilon_1'' - \epsilon_1')(\beta - 1)/RT} \tag{20}$$

where ϵ_1'' and ϵ_1' are values of the adsorption energy of the first component corresponding to sites having adsorption coefficients b_1'' and b_1'.

Equation 20 shows that, in the case under examination, b_2/b_1 may be the better approximated by means of some constant (within the range b_2'/b_1' to b_2''/b_1''), the lower the value of $(\epsilon_1'' - \epsilon_1')(\beta - 1)$ in comparison with RT. Again, for a given degree of accuracy in such an approximation, the less the difference in the adsorption energies of the two components, i.e. the nearer β is to unity, the less is the need for narrowness in the interval $\epsilon_1'' - \epsilon_1'$. In the limit, when $\beta = 1$, this interval may be as wide as we like. On the other hand, the narrower the interval $\epsilon_1'' - \epsilon_1'$, the less the limitations to the value of β. In the limit, when $\epsilon_1'' - \epsilon_1'$ is very small, β may have any value we like. In the general case, as already stated, the possibility of approximating b_2/b_1 by means of some constant is determined by two factors: an insignificant difference in energies of adsorption and a comparatively narrow "range of heterogeneity" over the main part of the surface. It was shown above that, if $b_2/b_1 \approx$ const, then Equations 14 and 15 are approximately true.

We consider that the case characterized by the condition:

$$(\epsilon_1'' - \epsilon_1')(\beta - 1) \leqslant RT \tag{21}$$

unlike the limiting cases already examined, is fairly frequently realized in practice.

This assertion, of course, cannot be proved directly, for we do not know the values of the local adsorption energies ϵ; in its support, however, we can advance a number of indirect arguments. Comparison of experimentally determined heats of adsorption for various gases on the same adsorbent and attempts to evaluate the relative local adsorption energies of different gases on a definite type of adsorption sites from the relative polarizabilities of these molecules show that the factor $(\beta - 1)$ very often has the value 0.1 - 0.3. With regard to the factor $(\epsilon_1'' - \epsilon_1')$, although its quantitative evaluation does not appear to be possible, there is reason to suppose that it is small for the adsorbents that are most important practically (active carbons, silica gels). For silica gels this conclusion follows from the experiments, for example, of Kiselev and coworkers [9] who showed that there was practically complete coincidence between the so-called "absolute" adsorption isotherms of nitrogen and other vapors on silica gels of differing origins and structures. As it is improbable that such different silica gels would have surfaces of identical heterogeneity, it must be considered that a substantial part of their surfaces is fairly homogeneous, which means, of course, that the difference $(\epsilon_1'' - \epsilon_1')$ is small.

For active carbons, the following considerations are presented as indirect confirmation of this point of view:

1. Adsorption isotherms for carbons can often be well described by interpolation formulas of the type $a = bp^{1/n}$; as is well known, the statistical theory of adsorption [2,3] leads in this case to an exponential distribution of the surface with respect to the values of local adsorption energies, i.e. to narrowness of the interval $\epsilon_1'' - \epsilon_1'$.

2. With increase in the degree of filling of the surface, the differential heats of adsorption (see, e.g. [8]) at first fall sharply, and the further filling of the surface then occurs very slowly. Although it is impossible to pass quantitatively from such a curve to the distribution function with respect to values of local adsorption energies, this is again a qualitative indication that over the main part of the surface the value of ϵ changes very little.

3. Analysis of the characteristic curves led Radushkevich [10] to the conclusion that active carbons, with respect to the dimensions of "elementary adsorption volumes" form extremely monodisperse systems. It appears to us that this conclusion is also in accord with the idea that over the main part of the surface the value of ϵ changes to an inappreciable extent.

It is to be regretted that there are practically no reliable experimental data on the adsorption of gas mixtures in the literature. In comparing, therefore, the results of the analysis made above with experiment, we are compelled to confine ourselves to our measurements [5,8] of the simultaneous adsorption of ethylene and carbon dioxide (at 25°) and of ethylene and propene (at 7° and 25°) on active carbon.

We will first point out that in all the systems studied the rule relating to rectilinear projection of the total adsorption isotheres on the plane $a_1 = 0$ is closely obeyed. Fig. 3 shows families of such projections for the case of ethylene–propene. On this figure partial pressures of ethylene are plotted along the axis of abscissa and those of propene along the axis of ordinates. The full lines represent the projections of the total adsorption isotheres for 7°, and the broken lines —for 25°. The number against each straight line indicates the value of the total adsorption for the given isothere in millimoles per gram. From our point of view the fact of the linearity of these isotheres is a consequence of the fact that in the systems that we have studied the condition of Equation 21 was realized.
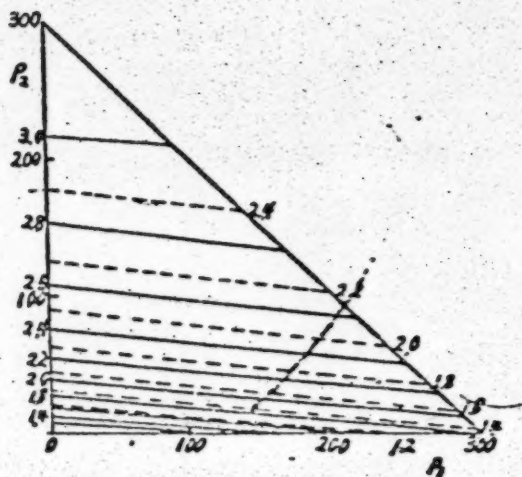
We will point out further that, as far as can be judged from the numerical data given in the paper of Lewis and coworkers [11] relating to the adsorption of binary gas mixtures, this rule applies also in the system studied by them. When this rule is obeyed, it is evidently very easy to construct the surface of total adsorption from the adsorption isotherms of the two pure components.

Fig. 3.

Contrary to the requirements of the approximate theory expounded above, the projections of the total adsorption isotheres are not parallel to one another. The absolute value of the slope of the experimental curve increases somewhat with rise in the degree of filling of the surface.

As was shown in our previous paper [8], the selectivity coefficient α_i remains practically constant along each isothere, as required by the approximate theory given above; but it falls somewhat with rise in the degree of filling of the surface.

From the point of view presented in this paper, it is easy to understand the cause of the increase, with rise in degree of filling, of the slope of the projections of the total adsorption isotheres; and also the cause of the decrease in the selectivity coefficient α_i. Actually, the lower the degree of filling, the greater must be the effect of the adsorption sites having the greatest adsorption energies. It is clear from a comparison of Equations 10 and 16 that the absolute value of the slope of the projection of an isothere on the plane $g_1 = 0$ must be the lower, the greater the effect of sites having high values of ϵ_2 (and therefore greater values of b_2).

Eliminating ϵ_2 from Equations 15 and 16, we find directly that sites having a higher value of ϵ_1 correspond to higher values of the selectivity coefficient α_i. With reduction in the degree of filling, therefore, the mean value of α_i over the whole surface must increase.

The approximate statistical theory given in this paper for the adsorption of binary gas mixtures is therefore in good semiquantitative agreement with the results of experiment. At the same time this theory cannot yet give a quantitative solution of the problem formulated at the beginning of the paper, for it does not indicate a method of calculating the selectivity coefficient α_i. In this connection, let us examine, in conclusion, the question of the possibility of an approximate estimate of the value of this coefficient from Equation 15.

Starting from the concepts of the simplest adsorption scheme of Langmuir, we may write

$$\frac{b_{1k}}{b_{1k}} \approx \sqrt{\frac{M_1}{M_2}} . \tag{22}$$

where M_1 and M_2 are the molecular weights of the adsorbed gases. As regards the value of $\epsilon_2 - \epsilon_1$, which enters into Equation 15, we may attempt to replace it approximately, for not too low degrees of filling, by the difference in the differential heats of adsorption q_i^o of the two pure components at identical degrees of filling:

$$\epsilon_2 - \epsilon_1 \approx q_2^o - q_1^o \tag{23}$$

There can be no doubt that this approximation is not particularly accurate, and it is permissible only in those regions where the curves of differential heats of adsorption against degree of filling have low slope. In favor of the soundness of such an approximation, we may argue that the difference $(q_2^o - q_1^o)$ automatically takes account of the part played by sites having higher values of adsorption energy, and that the use of this difference instead of $(\epsilon_2 - \epsilon_1)$ must therefore lead to the experimentally observed dependence of α_2 on the degree of filling.

Substituting Equations 22 and 23 in Equation 15, we obtain:

$$\alpha_2 \approx \sqrt{\frac{M_1}{M_2}} \ e^{(q_2^o - q_1^o)/RT} . \tag{24}$$

Using the values of q_2^o and q_1^o that we obtained for the adsorption of pure ethylene and pure propylene on carbon [3], we have calculated the value of α_2 for the system in which we are interested from Equation 24. This calculation gives a somewhat unexpectedly good agreement with experiment, as will be seen from the table.

a_2 (m-moles/g)	α_2 (Calcd)	α_2 (Found)
1.4	14.0	15.0
1.8	12.8	13.5
2.0	11.8	12.2

In spite of this agreement, we are not prepared to assert, as yet, that this method of calculation is of a sufficiently universal character

SUMMARY

1. An examination has been made of the general equations yielded by the theory of the adsorption of binary gas mixtures on heterogeneous surface in absence of interaction.

2. An indication has been given of those cases in which it is possible to calculate adsorption from mixtures from the known isotherms for the adsorption of the pure components, without intermediate determination of the distribution function.

3. A rule has been deduced relating to the rectilinear character of projections of isosteres for total adsorption on the plane $a_1 = 0$, and the limits of applicability of this rule have been indicated.

4. A method has been given for the approximate evaluation of values of selectivity coefficients in those cases in which the rule of rectilinear isotherms of total adsorption holds.

5. A comparison has been made of the conclusions obtained with the results of an experimental investigation of the adsorption of binary gas mixtures on active carbon, and it has been shown that there is good agreement between theory and experiment.

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ELUCIDATION OF THE ROLE OF DIFFERENT ADSORPTION CENTERS IN THE HYDROGENATION OF ACETYLENE OVER NICKEL

COMMUNICATION 2. INVESTIGATION OF THE KINETICS OF THE HYDROGENATION AND ACTIVATED ADSORPTION OF ACETYLENE AT A NICKEL CATALYST

N. P. Keier

In the first communication [1] we gave the results of an investigation of the active surface of a nickel catalyst with the aid of a differential isotopic method. The nickel studied was prepared, following Rug and Egupov's method, by the alkali leaching of a 50 % alloy of nickel with aluminum. Powerful activated adsorption of acetylene on the catalyst was observed at room temperature. A considerable part of the acetylene was adsorbed irreversibly i.e. could not, under any conditions, be removed from the surface as acetylene. When the temperature was raised to above 150°, apart from acetylene, appreciable amounts of hydrogen and methane were desorbed.

It was established, with the aid of the differential isotopic method, that the active surface was hetero-geneous with respect to activation energies for acetylene desorption. Catalytic reactions of different types occur on active adsorption centers differing in heats of adsorption and activation energies. The hydrogenation reaction is effected only on a small group of adsorption centers occupying 4-6% of the surface, and these adsorption centers comprise a part of those on which reversible adsorption occurs. Methane formation occurs at active centers corresponding to a lower degree of filling i.e. having higher heats of adsorption and lower activation energies. Decomposition of acetylene with separation of hydrogen and formation of a surface compound of the nickel carbide type occurs in the case of acetylene adsorbed on more active centers.

Investigation of the catalyst after several adsorption experiments with the aid of X-rays showed that it contains, apart from metallic nickel and residual aluminium oxide Al₂O₃, some nickel carbide Ni₃C [2] formed by reaction of acetylene with nickel.

In view of the established heterogeneity of the active surface, it was considered to be of interest to investigate the distribution of active centers according to their activation energies for the adsorption of acetylene and to determine the way in which the activation energy depends on degree of filling.

1. Determination of the Distribution Function for Active Adsorption Centers according to Activation Energies for the Adsorption of Acetylene.

In order to find the distribution function with all its associated constants, and also to find the variation in activation energy, measurements must be made of at least two kinetic isotherms at two temperatures [3].

Repeat experiments on the adsorption of acetylene on the same sample of catalyst never gave agreeing results. Fig. 1 shows kinetic adsorption curves for a series of successive experiments on one sample of catalyst. Between the experiments, activation by prolonged degassing at 10⁻⁶ mm Hg and 300-500° was carried out. As will be seen from the graph, adsorption at a freshly activated surface is more than 2.5 times that found in all succeeding experiments (Fig. 1). Increase of activation temperature to 500° did not improve the reproducibility of the active surface. Progressive poisoning of the catalyst occurred in the successive experiments.

The graphs in Fig. 1 show that the kinetic adsorption isotherms satisfy the equation previously found for the adsorption of many gases on various carbons, on nickelous oxide, and on other catalysts:

$$q = At^{1/n} \qquad (1)$$

where

$$1/n = \alpha RT, \tag{2}$$

and

$$A = \frac{H}{\alpha(\tau_0)^{\alpha RT}}. \tag{3}$$

α and H are constants characterizing the distribution of active sites according to activation energies:
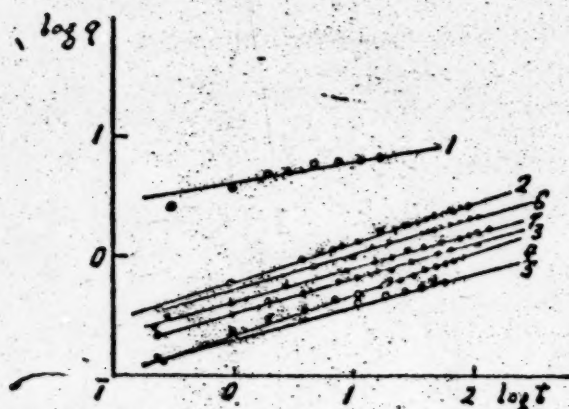$\rho(E) = He^{\alpha E}$ (4). As will be seen from Fig. 1, when several adsorption experiments are carried out on the same sample, poisoning is observed that has little effect on the slope of the curve representing the kinetics of adsorption in bilogarithmic coordinates. In Table 1 the values of log A and α for these experiments are given. It can be seen that α increases for a poisoned surface (in comparison with the first experiment), and then undergoes little change. H falls with poisoning. The absence in these experiments of an obvious relationship between changes in α and in A indicates that the fall of A is related to the fall in H. As it was impossible to carry out two reproducible experiments on the same sample, it was necessary to use a fresh sample of catalyst for each experiment. Identity of all conditions in the experiments was an essential prerequisite for the obtaining of reproducible results. Samples of 0.5 g were taken. The nickel was first dried for one hour at about 130-150° in a stream of nitrogen. The activation in these experiments was carried out under strictly constant conditions. The sample was degassed at 10^{-4} mm Hg at 300° for two hours, with a trap immersed in liquid nitrogen attached. Then, at the same temperature, the nickel oxides formed on the surface were reduced with hydrogen. At the end of the reduction process hydrogen was pumped off, the trap was

Fig. 1. Kinetics of the adsorption of acetylene in bilogarithmic coordinates log q and log t: 1) Expt. 1, freshly activated sample; 2) Expt. 2, sample from Expt. 1 activated at 350°, 10 hrs; 3) Expt. 3, same sample activated at 350, 1.5 hrs; 4) Expt. 4, same sample activated at 350°, 1 hr; 5) Expt. 5, same sample activated at 350°, 1 hr; 6) Expt. 6, same sample activated at 500°, 1 hr; 7) Expt. 7, same sample activated at 500°, 1 hr.

removed for a period of 20 minutes from the liquid air in order to remove the water that had condensed, and it was then placed in solid carbon dioxide. The final degassing of the catalyst was carried out at 500° under the vacuum from a mercury condensation pump for one hour. Fig. 2 shows two kinetic adsorption isotherms obtained at 0° and 19.5° at the same pressure.

The constants characterizing the kinetic curve, which are found from the slopes of the kinetic curves in bilogarithmic coordinates, are given in Table 2.

From the displacement of the kinetic isotherms measured at 0° and 19.5° along the coordinate RT log t, the constant log τ_0 was determined (-9.75). With the aid of the constants α, log τ_0 and A, the constants characterizing the distribution function of active centers according to their activation energies for the adsorption of acetylene were found [4]. The complete form of the distribution function is expressed by the equation

$$\rho(E) = 2.13 \cdot 10^{-11} e^{2.63 \cdot 10^{-4} E} \ (cal/mole)^{-1} \tag{5}$$

The variation in activation energy with the adsorption, found from Roginsky's equation [3], is given in Fig. 3. The activation energy rises from 11 to 18 kcal/mole when adsorption changes from 0.256 to 2.56 ml/g.

TABLE 1

Expt. No.	Pressure (mm Hg)	Temp. (°C)	log A	α (cal/mole)$^{-1}$	Activation conditions
1	5.88	22.2	0.6	$2.8 \cdot 10^{-4}$	Freshly prepared sample degassed at 300° for 1 hr.
2	2.67	25.6	$\overline{1}$.78	$5.8 \cdot 10^{-6}$	At 360° for 10 hrs.
3	2.77	25.5	$\overline{1}$.52	$5.0 \cdot 10^{-4}$	At 350° 1.5 hrs.
4	2.67	25.9	$\overline{1}$.37	$5.7 \cdot 10^{-6}$	At 350° 1 hr.
5	2.84	25.7	$\overline{1}$.30	$4.0 \cdot 10^{-4}$	At 350° 1 hr.
6	2.77	25.5	$\overline{1}$.72	$5.0 \cdot 10^{-4}$	At 500° 1 hr.
7	5.39	25.0	$\overline{1}$.62	$4.7 \cdot 10^{-6}$	At 500° 1 hr.

Fig. 2. Kinetics of the adsorption of, acetylene on a sample of previously dried nickel: 1) Expt. 8 ($\overline{1}$ 0°, P 4.478 mm Hg); 2) Expt. 9 ($\overline{1}$ 19.5°, P 4.355 mm Hg).

2. Comparison of the Rate of Adsorption of the Reaction Components with the Rate of Hydrogenation of Acetylene

There are indications in the literature that in a number of cases, in particular for the hydrogenation of ethylene on nickel, complete adsorption is a stage in which the active centers are removed from the catalytic reaction, and the hydrogenation reaction proceeds in the pre-adsorption state [5]. It was necessary to verify whether hydrogenation proceeds in our case by this mechanism as well as by the adsorption mechanism, for the hydrogenating group of active centers that we have found might then be only a small proportion of the catalytically active centers. Coincident or nearly coincident values of the initial rates of adsorption and hydrogenation would be an almost unequivocal proof of the presence of an adsorption mechanism, whereas a much higher value for the initial rate of hydrogenation would be evidence for the other mechanism.

TABLE 2

Expt. No.	Temp. (°C)	Pressure (mm Hg)	α RT	$\alpha \cdot 10^4$ (cal/mole)$^{-1}$	log A
8	19.5±0.1	4.55	0.25	4.37	−0.26
9	19.5±0.1	4.35	0.23	3.86	−0.26
10	0	4.48	0.21	3.85	−0.41
11	0	4.48	0.21	3.85	−0.41

In order to verify this hypothesis we have carried out experiments that permit an estimation of the rates of the initial stages of these processes. The initial rate of the process (expressed as the reduction in volume per minute per gram of catalyst) on admitting a mixture of acetylene and hydrogen (1:2) to freshly activated catalyst is 1.53 ml per min per g (Expt. 18). The initial rate of adsorption of acetylene, also on a freshly activated nickel surface, is 1.57 ml per min (Expt. 19). The close values of the initial rates in these experiments, however, cannot be regarded as a proof of the adsorption mechanism of hydrogenation, for it was found that in Expt. 18, in addition to hydrogenation, there occurred also rapid irreversible adsorption of acetylene. In Expt. 18 the irreversible adsorption of acetylene amounted to 3.06 ml/g, and in Expt. 19 2.55 ml/g was adsorbed at equilibrium. In order to estimate the true initial value of the rate of hydrogenation, comparative experiments were carried out on hydrogenation and adsorption over a sample of catalyst over which a preparatory adsorption of acetylene and hydrogen had been carried out, the sample being then degassed at room temperature, when a part of the reversibly adsorbed acetylene and hydrogen was removed from the surface.

In Fig. 4, Curve 1 represents the kinetics of the hydrogenation of acetylene in a 1:2 mixture at room temperature (Expt. 20, Table 3). After the hydrogenation the sample was again degassed at room temperature and adsorption of acetylene was allowed to occur on it (Expt. 21) at a pressure of 1.01 mm Hg. identical with the partial pressure of the acetylene in the hydrogenation experiment (Expt. 20). The kinetics of adsorption are represented by Curve 2 of Fig. 4. Comparison of the initial rates of the two processes shows that they are close in value. In the first five seconds, the pressure in Expt. 20 (on hydrogenation) fell by 0.26 mm Hg and in one minute by 1.005 mm Hg. In the adsorption experiment in the first five seconds the pressure fell by 0.226 mm Hg, and in one minute by 0.784 mm Hg. It will be seen that in this case the initial rate of hydrogenation
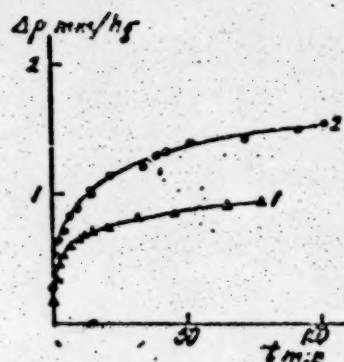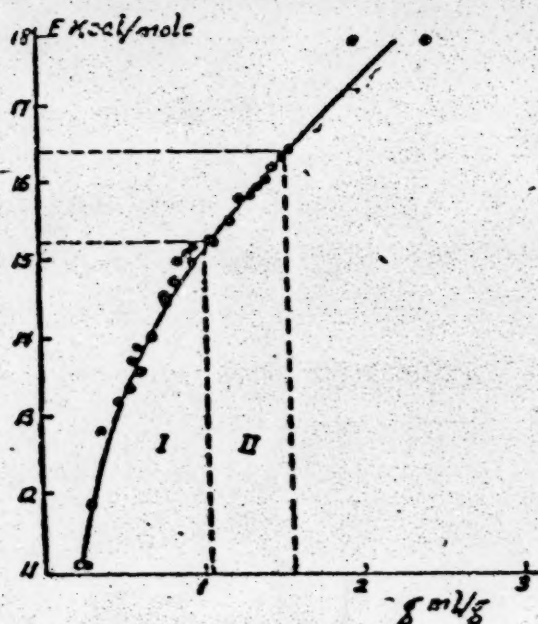
Fig. 3. Variation in activation energy of adsorption of acetylene with the degree of adsorption on a sample of previously dried nickel.
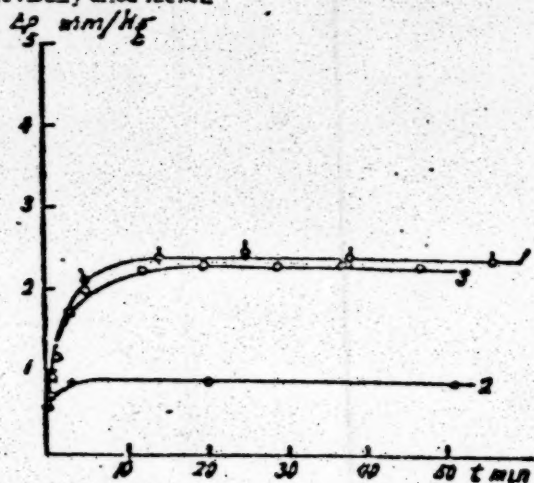

Fig. 4. Kinetics of the hydrogenation of acetylene expressed as the fall in pressure in the reactor per gram of catalyst: 1) Expt. 20, hydrogenation at room temp. on surface degassed after adsorption of acetylene at room temp.; 2) Expt. 21, adsorption of acetylene on sample from Expt. 20, degassed at room temp.; 3) hydrogenation at room temp. on the same sample degassed at room temp. after Expt. 18-21.

does not exceed the rate of adsorption. In the course of time, as will be seen from Fig. 4, the rate of hydrogenation begins to overtake the rate of adsorption, because the hydrogenating surface is being continually renewed. Slowing down occurs in this case only as the components in the original mixture are used up. In Expt. 20, altogether 61% of the acetylene was hydrogenated, the remaining acetylene was adsorbed. Of the hydrogen also, only 57% was used in hydrogenation, the remaining 43% being adsorbed. The amount of adsorbed hydrogen was about twice as great as in Expt. 18, in which adsorption of the hydrogen was carried out at a freshly activated surface under a pressure about three times as great as that of Expt. 20 (Table 3).

The incomplete utilization of acetylene for hydrogenation could result either owing to simultaneous adsorption of acetylene on centers inactive for hydrogenation, or at the end of the process, owing to insufficiency of hydrogen at hydrogenating centers (resulting from its more rapid adsorption). As the pressure of hydrogen in the mixture increases, the amount of adsorbed hydrogen increases (Table 5, Expts. 28-31) and that of acetylene falls, not however to zero. This fact is evidence that the process of the adsorption of acetylene proceeds simultaneously with hydrogenation at catalytically inactive centers, thus removing acetylene from reaction. Expts. 20, 28, and 29 show also that the rate of adsorption of hydrogen under these conditions is of the same order as that of the hydrogenation reaction. In experiments with 1:2 mixtures of acetylene and hydrogen, owing to the shortage of hydrogen due to its partial adsorption, there is an increased amount of adsorbed acetylene. Experiments 22-24 (Fig. 5, Table 3) show the effect of temperature on the rate of hydrogenation. It can be seen that there is no appreciable effect on the rate of the process resulting from rise in temperature up to 100°. With rise in temperature from 19° to 100° the amount of adsorbed acetylene falls from 37 to 25%, and that of hydrogen from 39 to 32%; the amount of hydrogenated acetylene rises from 61 to 70%. The residual pressure

TABLE 3

Expt. No.	Pressure of acetylene (P_a) (mm Hg)	Pressure of hydrogen (P_b) (mm Hg)	Temp. (°C)	Acetylene (mm Hg)			Hydrogen (mm Hg)		
				hydrogenated	adsorbed	remaining	hydrogenated	adsorbed	remaining
33	—	6.068	19	—	—	—	—	0.547	5.521
19	2.927	—	19	—	3.875	0.442	—	—	—
20	1.05	2.24	19	0.64	0.39	0.009	1.28	0.96	0
21	1.01	—	19	—	0.933	0.078	—	—	—
22	0.91	2.03	48	0.635	0.23	0.04	1.27	0.76	—
23	0.794	1.693	100	0.547	0.198	0.049	1.094	0.546	0.053
24	1.05	2.568	20	0.636	0.385	0.01	1.33	0.995	0.243
25	0.179	0.427	19	0.078	0.101	—	0.156	0.244	0.027
26	1.204	0.36	20	0.168	1.036	—	0.336	0.024	—
27	1.794	0.362	19	0.329	1.455	—	0.65	—	—
28	0.38	0.681	10	0.205	0.153	0.022	0.41	0.271	—
29	0.38	0.681	19	0.205	0.153	0.022	0.41	0.271	—
30	0.373	1.502	20	0.32	0.053	—	0.34	0.492	0.369
31	0.362	3.604	19	0.283	0.068	0.011	0.566	0.948	2.09
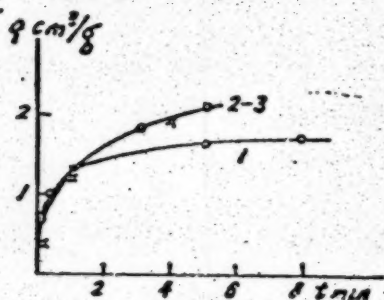
Fig. 5 Dependence of the kinetics of the hydrogenation of acetylene in a 1:2 acetylene –hydrogen mixture on temperature: 1) Expt. 23 (T 100°, P of mixture 2.487 mm Hg); 2) Expt. 22 (T 48°, P of mixture 2.94 mm Hg); 3) Expt. 20 (T 19.5°, P of mixture 3.29 mm Hg).

of acetylene and hydrogen rises (Expt. 23, Table 3). Increase in the partial pressure of acetylene (Expts. 25 and 26) lowers the degree of adsorption of hydrogen, probably owing to the rise in the rate of hydrogenation. When there is an excess of acetylene, a part of the hydrogen previously adsorbed on the surface is utilized.

The following conclusions can be drawn from this series of experiments: 1) hydrogenation of acetylene passes through the stage of complete adsorption; 2) in addition to hydrogenation adsorption, which removes acetylene and hydrogen from the reaction, takes place (the adsorption of acetylene under these conditions is in accord with the fact that not all centers that reversibly adsorb acetylene are hydrogenating centers); 3) adsorption of hydrogen increases in presence of adsorbed acetylene; 4) the catalytic activity does not change in repeat experiments. 5) with rise in temperature, the minimum pressure of acetylene necessary for hydrogenation rises; 6) adsorption of hydrogen in presence of acetylene is higher than at a clean surface.
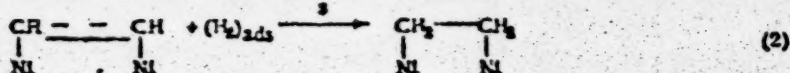
3. Discussion of Results

The results given in this communication taken together with those given in the first communication permit us to draw certain conclusions concerning the mechanism of the hydrogenation of acetylene and the formation of methane at a nickel surface.

a) Hydrogenation of Acetylene. As has been shown, the hydrogenation of acetylene passes through the stage of complete adsorption. Catalytic activity is confined to a small group of adsorption centers occupying about 4-6% of the surface. This group of active centers is characterized by definite values of activation energies and heats of adsorption. On a sample of low activity hydrogenation proceeds at active centers having activation energies of 15-16 kcal/mole; on an active sample the values are lower.

Experiments with the differential isotopic method have shown that hydrogenation proceeds on a fraction of the active centers on which reversible adsorption of acetylene occurs. The first hydrogenated portion of acetylene

is in all cases close in composition to the first portion of acetylene desorbed at room temperature. This implies that hydrogenation occurs at a group of active centers having minimum, or almost minimum, activation energies for desorption (Fig. 6, shaded region bc). Hydrogenation does not occur at active centers having higher activation energies of adsorption.

It might be supposed that one of the conditions for hydrogenation would be the geometric proximity of acetylene and hydrogen adsorption centers. Account must be taken also of the fact that in experiments in which hydrogen is adsorbed first and then the catalyst is brought into contact with acetylene, only a small amount of product, mainly ethylene, is formed. This is evidence that the mechanism of hydrogenation of adsorbed acetylene includes a stage of interaction with free hydrogen.

The mechanism of hydrogenation has been frequently discussed in the literature, mainly on the basis of the example of ethylene. The hydrogenation of acetylene is more complicated. We shall attempt to give a mechanism that will be consistent with our observations. The first stage is the reversible adsorption of acetylene with opening of one link and the weakening of a second:

$$C_2H_2 \underset{2}{\overset{1}{\rightleftarrows}} \begin{array}{cc} CH = CH \\ | \quad\quad | \\ Ni \quad\quad Ni \end{array} \tag{1}$$

The second stage is the interaction of adsorbed acetylene with hydrogen adsorbed on neighboring active centers:

$$\begin{array}{cc} CH - - CH \\ | \quad\quad | \\ Ni \quad . \quad Ni \end{array} + (H_2)_{ads} \overset{3}{\longrightarrow} \begin{array}{cc} CH_2 - CH_2 \\ | \quad\quad | \\ Ni \quad\quad Ni \end{array} \tag{2}$$

In this stage an intermediate complex is formed which corresponds to ethylene in composition. This complex may either be converted into ethylene and pass into the gas phase, or undergo further reaction with hydrogen adsorbed from the gas phase on a liberated active center:

$$\begin{array}{cc} CH_2 - CH_2 \\ | \quad\quad | \\ Ni \quad\quad Ni \end{array} \overset{4 \nearrow C_2H_4}{\underset{5 \;\; +(H_2)_{ads}}{\longrightarrow}} C_2H_6 \tag{3}$$
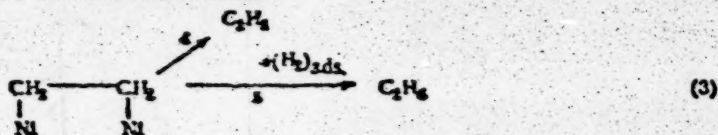
In our case, owing to the presence of an excess of hydrogen, Reaction 5 proceeds more rapidly than Reaction 4 and determines the ratio of ethylene and ethane. With rise in temperature, the rate of the back reaction (2) increases more rapidly than that of the forward one; for this reason the apparent temperature coefficient of the hydrogenation reaction is zero or even negative. It may be considered that the cause of the nonoccurrence of hydrogenation at some of the active centers that reversibly adsorb acetylene is the need for a definite degree of weakening in the double bond, which does not occur at the less active centers.
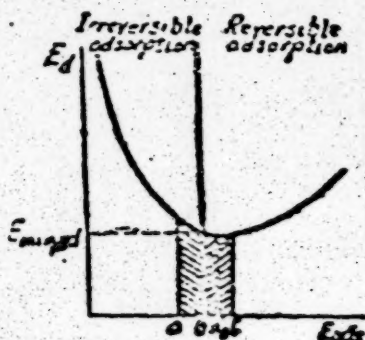
b) Mechanism of the Formation of Methane. Formation of methane over the investigated catalyst occurs only above 150°. Formation of methane occurs both in presence of hydrogen in the gas phase, and also in its absence, owing to the redistribution of the hydrogen of the acetylene. By the use of labeled methane it was found possible to show that methane is formed on a definite group of active adsorption centers characterized by intermediate values of activation energy. Formation of methane occurs at active centers having lower E_{ads} values than those for centers at which reversible adsorption of acetylation occurs (see Fig. 6, shaded region ab).

Fig. 6. Form of the curve for activation energy of desorption E_d against activation energy of adsorption: region ab) methane-forming centers; bc) hydrogenating centers.

The first stage of this reaction is the adsorption of acetylene. Being adsorbed on active centers differing in heats of adsorption, the acetylene molecules suffer internal bond breakdown in differing degrees. On active centers having low heats of adsorption and high energies of activation, the bond between the carbons of the acetylene molecule remains stronger than that between carbon and nickel atoms: on these active centers reversible adsorption of acetylene occurs. On active centers having higher heats of adsorption there are stronger bonds between carbon and nickel atoms, comparable with those between the carbons of the acetylene molecule. With increase in temperature, further strengthening of the bond between nickel and carbon occurs at these active centers, and it finally passes over into a carbide type of bond, the hydrogen being either adsorbed on neighboring active centers, or given up to the gas phase.

Reaction of the surface nickel carbide with hydrogen at a temperature of above 300° leads to the formation of methane. Formation of methane (also from adsorbed acetylene) at 150-200° proceeds by another mechanism on centers that are less active than those just discussed. We give below a scheme of processes leading to the formation of methane at this group of active centers:

$$CH \equiv\!\equiv\!\equiv CH \longrightarrow \underset{Ni}{CH} - \underset{Ni}{CH} \qquad (1)$$

$$\underset{Ni}{CH} - \underset{Ni}{CH} + H_2 \longrightarrow \underset{Ni}{CH_2} - \underset{Ni}{CH_2} \qquad (2)$$

$$\underset{Ni}{CH_2} - \underset{Ni}{CH_2} + H_2 \longrightarrow \underset{Ni}{CH_3} \; \underset{Ni}{CH_3} \qquad (3)$$

$$\underset{Ni}{CH_3} \; \underset{Ni}{CH_3} + H_2 \longrightarrow 2CH_4 \qquad (4)$$

The first stage is the adsorption of acetylene on account of the breakdown of one of the π-bonds. A second bond then becomes unstable, and the state of the molecule approximates to that of a radical, so that hydrogen readily combines with it; evidence for this is to be found in the increased adsorption of hydrogen in presence of acetylene adsorbed on the surface. The second stage, therefore, occurs rapidly in presence of free or adsorbed hydrogen at room temperature. It should be noted that the high strength of the bond between carbon and nickel atoms at this group of active centers excludes the possibility of desorption of ethylene molecules from them. The third and fourth stages occur only at elevated temperature, for the action of hydrogen on adsorbed acetylene at room temperature does not lead to formation of methane. In absence of a supply of hydrogen from without, these reactions occur by the aid of hydrogen separating above 150° by the reaction:

$$3(C_2H_2)_{ads} \longrightarrow 6Ni_3C + 3H_2 \qquad (5)$$
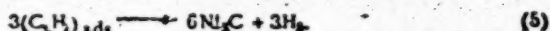
It is characteristic that methane and hydrogen always appear simultaneously in these experiments. The formation of hydrogen occurs, evidently, at the surface, and not in the gas space, for in our experiments the desorbed gas was removed from the reactor space into another space with the aid of a circulation pump so that the gas pressure above the catalyst during desorption did not exceed 10^{-4} mm Hg. Poisoning due to the adsorption process, which was observed after the first adsorption experiment, is probably associated with Reaction 5. The active surface is not restored by activation at 500°. This carbon is only partially removed in presence of hydrogen at temperatures of above 300° (in the form of methane). Methane formation was observed also in the repeat experiments, but on a reduced scale, thus indicating that, as a result of the reaction, methane-forming centers are freed. This is in accord with the proposed mechanism.

SUMMARY

1. Adsorption centers differing in their heats of adsorption and activation energies differ also in their catalytic properties. The hydrogenation and methane-forming reactions of acetylene occur at different groups of active centers, differing in their heats of adsorption and activation energies.

2. A mechanism has been proposed for hydrogenation in which the first stage is the reversible chemical adsorption of acetylene.

3. Methane formation occurs by two processes, one of which proceeds at a higher temperature via the reduction of a nickel carbide, and the other proceeds by the splitting of a partially hydrogenated adsorbed acetylene

molecule at the carbon—carbon linkage, followed by addition of a hydrogen molecule. The first process occurs at active centers having very high heats of adsorption, and the second occurs at active centers having lower heats of adsorption.

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• See Consultants Bureau English translation, page 577.

SYSTEMS CONTAINING CONCENTRATED HYDROGEN PEROXIDE

COMMUNICATION 3. SOLUBILITY ISOTHERMS FOR THE TERNARY SYSTEM: $CO(NH_2)_2$–H_2O_2–H_2O

S. Z. Makarov and B. A. Lebedev

In 1875, Shene [1], professor at the Moscow Agricultural Academy, found that hydrogen peroxide can combine with a number of metal dioxides, forming double compounds, e.g. $K_2O_2 \cdot 2H_2O_2$, $BaO_2 \cdot 2H_2O_2$, etc. – the so-called perhydrates. Numerous investigators have since shown that compounds of this type are formed not only by metal peroxides, but also by many salts, weak bases, and certain organic compounds having the properties of weak bases. The study of compounds of this class proceeded, however, entirely by preparative methods. In the present investigation, unlike previous investigations (if we disregard that of Janecke [2]), the conditions are determined for the synthesis of $CO(NH_2)_2 \cdot H_2O_2$ in the ternary system $CO(NH_2)_2$–H_2O_2–H_2O.
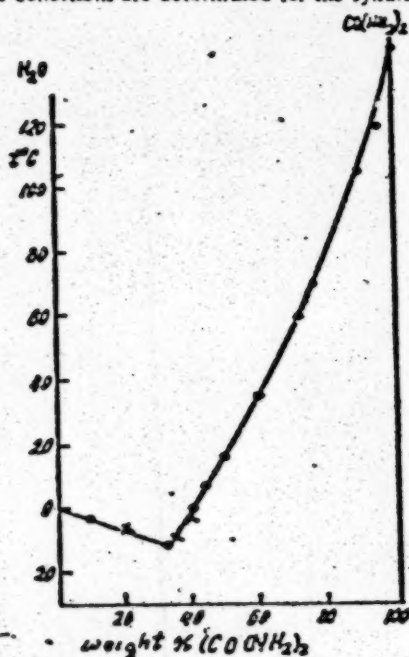
Fig. 1. The system $CO(NH_2)_2$–H_2O. o) Janecke's results; x) Blindin's results.

The binary system, $CO(NH_2)_2$–H_2O has been studied by several authors [3,4,5,6,7] from 1902 onwards. The investigations of Janecke [6] and Blindin [7] are the most interesting. Janecke studied the course of the urea solubility curve, starting from the eutectic point and finishing with a solution containing 95% of urea. The eutectic of the system occurs at $-11.5°$ at a concentration of 32.5% urea. The curve for the solubility of urea is featureless, thus indicating the absence of any hydrates or polymorphous modifications of urea. Blindin [7] found one point on the ice curve and two on the urea curve, thus permitting a determination of the position of the eutectic point, which was in good agreement with that found by Janecke. Thus, these solubility data practically define the whole of the binary system $CO(NH_2)_2$–H_2O over the whole concentration range of both components up to the melting point of urea, $132.5°$ (Fig. 1).

Information on the second binary system H_2O_2–H_2O began to appear in the literature in 1900 [8,9,10,11,12,13]. In 1920 Maass and Herzberg [10] studied the liquidus line of the H_2O_2–H_2O system by the visual method and showed that the chemical compound $H_2O_2 \cdot 2H_2O$ is formed. In 1940 Giguere and Maass [12] confirmed these results and supplemented them by a study of the solidus line; they showed that solid solutions were formed in the system by all the solid phases.

The fact that ice and hydrogen peroxide form solid solutions is in contradiction with the existing concepts concerning the possibility of forming solid solutions of ice. In 1950 Kubaschewski and Weber [13], in a more accurate determination of the transition points of this system with the aid of cooling and heating curves, determined the positions of the liquidus and solidus curves and confirmed Giguere and Maass's results concerning the presence in the system of pairs of solid solutions.

In February 1951, however, a paper appeared by Foley and Giguere [14] in which the existence of solid solutions of water in hydrogen peroxide and of hydrogen peroxide in water is completely rejected. The composition of the solid phases was determined by the method of the third indifferent component: potassium chloride. In order to prevent completely any possible displacement of the equilibrium between water and hydrogen peroxide owing to the presence of an appreciable amount of potassium chloride, the authors repeated their experiments, using the method of labeled atoms. As the third component they used radioactive phosphorus P^{32} (in the form of potassium dihydrogen phosphate KH_2PO_4), which in many respects was quite suitable for this purpose. The results of these experiments coincided with those previously obtained and confirmed the absence of solid solutions in the system $H_2O-H_2O_2$. Independently of this work, Mironov and Bergman [15] who determined cooling and heating curves by the visual method with great accuracy, also established the absence of solid solutions in this system (Fig. 2).

There are no data for the system $CO(NH_2)_2-H_2O_2$. Tanatar [16] first obtained the compound of urea with hydrogen peroxide $CO(NH_2)_2 \cdot H_2O_2$ in Russia in 1908. There is a wide patent literature on urea perhydrate and its preparation under laboratory and industrial conditions.
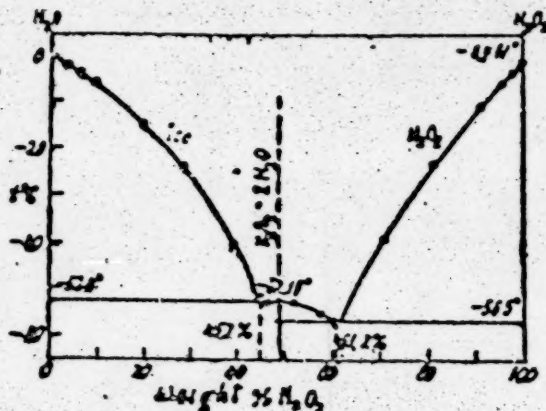
Fig. 2. Binary system $H_2O_2-H_2O$.

The ternary system $CO(NH_2)_2-H_2O_2-H_2O$ was investigated by Janecke [2] in 1932 by the visual observation of the separation of the first crystals from aqueous solutions of urea and hydrogen peroxide in given proportions across sections of the ternary system. Janecke took 11 sections with solutions of 3-62% of H_2O_2 and 5-60% of urea. From the results from these sections Janecke constructed a diagram for the ternary system, predominantly in the ice and urea perhydrate regions, and partially in the urea region (Fig. 3). The results obtained by such a method make it possible to construct a diagram that is sufficiently accurate as a first approximation. The method chosen did not permit a direct determination of the composition of the liquid phase at the transition points of the system, and these points can therefore be considered to be known only approximately.

EXPERIMENTAL

We investigated the ternary system $CO(NH_2)_2-H_2O_2-H_2O$ by the isothermal method at three temperatures: 0, 5, and 10°. The procedure consisted in the preparation of a saturated solution which was in equilibrium at the given temperature with its corresponding solid phase, the permitted limits of temperature variation being $\pm 0.1°$. Equilibrium was established under good stirring in 1-4 hours, depending on the H_2O_2 content of the liquid phase. The criterion of the attainment of equilibrium was constancy of hydrogen peroxide concentration in two consecutive tests on the liquid phase.

Analysis of the liquid phase and the residue for hydrogen peroxide was carried out iodometrically, and urea was determined by conversion into ammonia followed by Kjeldahl distillation. The composition of the solid phases was determined graphically by the method of residues. The starting materials were urea of the firm of Schering, carefully purified by recrystallization, and hydrogen peroxide completely freed from stabilizers and concentrated in a vacuum to an H_2O_2 content of 70-80%.

In experiments in which a greater concentration of hydrogen peroxide was required in the liquid phase we used urea perhydrate in place of urea, the perhydrate being prepared by the action of perhydrol on crystalline urea at 0°. This product, after being dried between filter papers in the air had practically the exact hydrogen peroxide content that is theoretically required for $CO(NH_2)_2 \cdot H_2O_2$. When kept for a long time in absence of stabilizer, it slowly decomposed, with separation of hydrogen peroxide, and deliquesced.

The results of the investigations of the ternary system for the three temperatures, 0, 5, and 10°, are shown in the table in the diagrams (Figures 4, 5 and 6).

TABLE

Results of the Investigation of the System $CO(NH_2)_2-H_2O_2-H_2O$ at 0, 5 and 10°

Point No	Comp. of liquid phase (% by wt.)			Comp. of residue (% by wt.)			Solid phase
	$CO(NH_2)_2$	H_2O_2	H_2O	$CO(NH_2)_2$	H_2O_2	H_2O	
				$t = 0°$			
1	39.98	—	60.02	—	—	—	$CO(NH_2)_2$
2	38.07	3.00	58.93	79.33	0.76	19.91	$CO(NH_2)_2$
3	47.81	5.92	46.27	90.39	10.17	—	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
4	47.80	6.02	46.18	83.08	6.33	10.59	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
5	48.22	5.98	45.80	86.19	8.00	5.81	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
6	42.38	5.30	52.32	59.10	30.28	10.62	$CO(NH_2)_2 \cdot H_2O_2$
7	19.33	13.78	66.89	59.92	28.60	11.48	$CO(NH_2)_2 \cdot H_2O_2$
8	20.52	15.29	64.19	58.51	32.27	9.21	$CO(NH_2)_2 \cdot H_2O_2$
9	17.24	16.31	66.45	57.07	32.40	10.53	$CO(NH_2)_2 \cdot H_2O_2$
10	12.71	37.20	50.09	54.93	34.47	10.60	$CO(NH_2)_2 \cdot H_2O_2$
11	9.71	56.19	34.10	57.25	37.84	4.91	$CO(NH_2)_2 \cdot H_2O_2$
				$t = 5°$			
	44.0	0.0	56.00	from solubility diagram			$CO(NH_2)_2$
1	30.86	2.02	47.12	93.62	0.34	6.04	$CO(NH_2)_2$
2	51.96	6.27	41.77	—	3.67	—	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
3	51.22	6.28	42.50	90.1	4.98	4.92	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
4	28.04	12.61	59.35	58.02	29.56	12.42	$CO(NH_2)_2 \cdot H_2O_2$
5	15.94	18.98	65.08	53.00	32.23	14.73	$CO(NH_2)_2 \cdot H_2O_2$
6	14.36	27.27	58.37	60.22	34.16	5.62	$CO(NH_2)_2 \cdot H_2O_2$
7	9.22	62.73	28.05	40.40	37.63	11.07	$CO(NH_2)_2 \cdot H_2O_2$
				$t = 10°$			
1	47.88	—	52.12	—	—	—	$CO(NH_2)_2$
2	47.87	—	52.13	—	—	—	$CO(NH_2)_2$
3	51.84	5.79	42.37	77.18	2.94	19.88	$CO(NH_2)_2$
4	53.26	6.98	39.76	68.08	18.37	13.35	$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2$
5	40.21	9.03	50.76	63.76	34.83	1.41	$CO(NH_2)_2 \cdot H_2O_2$
6	34.25	11.44	54.31	56.73	30.34	12.93	$CO(NH_2)_2 \cdot H_2O_2$
7	15.33	25.11	59.56	60.02	35.19	4.79	$CO(NH_2)_2 \cdot H_2O_2$
8	17.81	28.34	53.85	56.52	34.92	8.93	$CO(NH_2)_2 \cdot H_2O_2$
9	9.48	57.74	32.78	56.84	39.12	4.04	$CO(NH_2)_2 \cdot H_2O_2$
10	11.56	70.51	17.93	57.50	40.03	2.47	$CO(NH_2)_2 \cdot H_2O_2$

The solubility isotherms for the system $CO(NH_2)_2 - H_2O_2 - H_2O$ are characterized by the presence of two branches, corresponding to the equilibrium conditions for the solid phases $CO(NH_2)_2$ and $CO(NH_2)_2 \cdot H_2O_2$. Over the concentration range studied, up to 60-70% H_2O_2 in the liquid phase, no other urea compounds containing a greater amount of chemically combined-hydrogen peroxide were detected.

Up to a content of approximately 5-7% H_2O_2, the solubility of urea rose to 48-64% along the branch corresponding to the conditions for the separation of $CO(NH_2)_2$. At higher concentrations of H_2O_2 the solubility of urea fell sharply, to approximately 10%, and the equilibrium solid phase became urea perhydrate $CO(NH_2)_2 \cdot H_2O_2$. The transition points on the isotherms corresponding to the presence of two solid phases
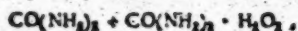
$$CO(NH_2)_2 + CO(NH_2)_2 \cdot H_2O_2 .$$

varied in composition to a comparatively insignificant extent over the temperature range studied.
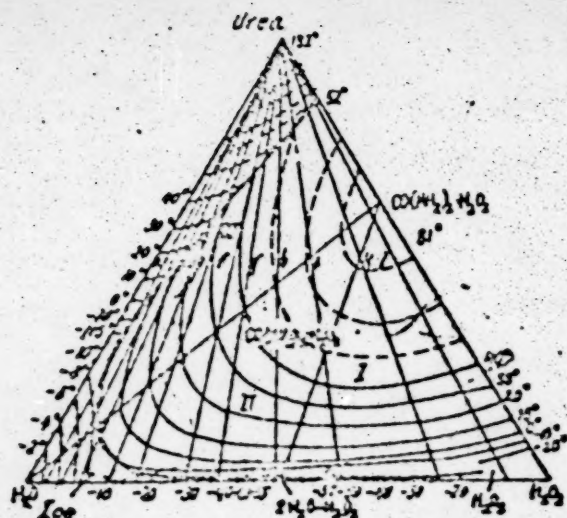
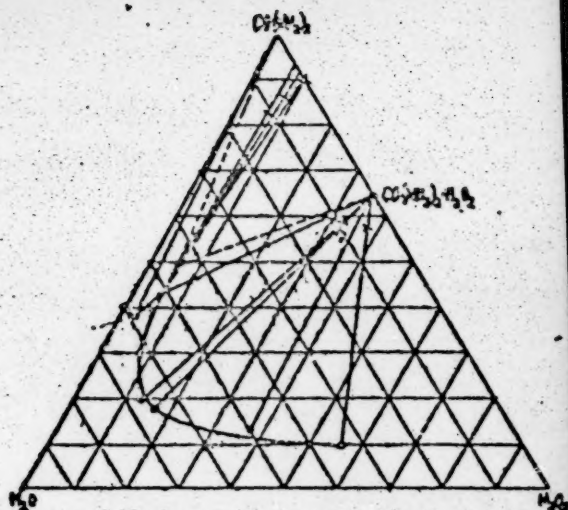Fig. 3. The ternary system $CO(NH_2)_2-H_2O_2-H_2O$ (according to Janecke).
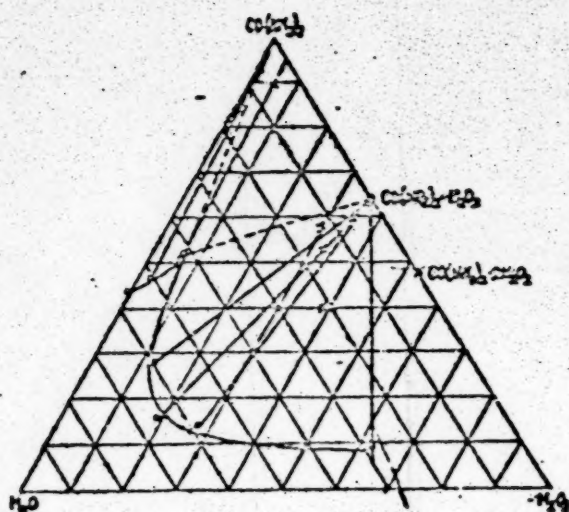

Fig. 4. 0° Isotherm for the system $CO(NH_2)_2-H_2O_2-H_2O$

Fig. 5. 5° Isotherm for the system $CO(NH_2)_2-H_2O_2-H_2O$.
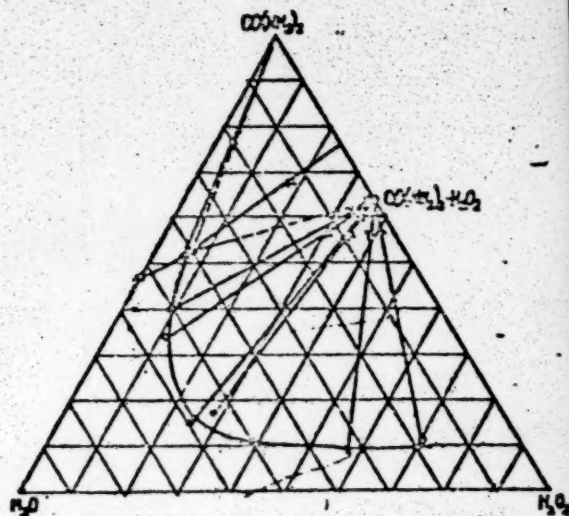
Fig. 6. 10° Isotherm for the system $CO(NH_2)_2-H_2O_2-H_2O$.

	0°	5°	10°
$CO(NH_2)_2$	42.8	51.6	53.3
H_2O_2	6.0	6.3	7.0

The obtaining of solubility data for H_2O_2 concentrations in the liquid phase of higher than 70% presents certain difficulties: the solutions become unstable, and decomposition of hydrogen peroxide becomes appreciable.

When the isotherms obtained for 0, 5, and 10° are compared with data from Janecke's isotherms, derived graphically from polythermal sections, discrepancies are clearly revealed. In the $CO(NH_2)_2$ and H_2O_2 concentrations Janecke's isotherms fall appreciably behind those obtained by the isothermal method. It is clear that this phenomenon is due exclusively to the absence of true equilibrium, owing to the rapid crystallization of the solid phases on cooling solutions of urea and hydrogen peroxide in studies by the polythermal method.

SUMMARY

1. The system $CO(NH_2)_2$-H_2O_2-H_2O has been studied by the solubility method at 0, 5 and 10°.

2. For H_2O_2 concentrations in the liquid phase of up to 70%, isotherms are characterized by the presence of two branches, corresponding to two solid phases: $CO(NH_2)_2$ and $CO(NH_2)_2 \cdot H_2O_2$.

3. Urea perhydrate $CO(NH_2)_2 \cdot H_2O_2$, so called "solid perhydrol", contains about 17.0% of active oxygen and is congruently soluble in water. In a number of cases its aqueous solutions can be used as solutions of hydrogen peroxide.

4. On the branch for saturation with $CO(NH_2)_2 \cdot H_2O_2$ there is a characteristic sharp fall in solubility of urea from about 50 to about 10%. Hydrogen peroxide at concentrations of greater than 5-7% has a salting out action on urea.

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HYDRATED CALCIUM SILICATES

N. A. Toropov, A. I. Borisenko, and P. V. Shirokova

Hydrated calcium silicates have for a long time occupied the attention of investigators, and the search for rational methods for the preparation of these compounds has been the subject of a large number of investigations. The interest shown in these compounds results from a number of causes. First of all, study of the conditions of formation of hydrated calcium silicates may permit us to understand the very complex mechanism of the hydration of Portland cement, the main components of which are calcium silicates. A knowledge of the chemistry of hydration, which causes the setting and hardening of cements, is of interest to technologists of the cement and building industries. Not less important is a knowledge of the processes of formation of hydrated calcium silicates for deciding the question of the desirability of the micronization of cements, which is now generally considered to determine not only the periods of setting and hardening of cements, but also the final strength of the cement "stone". Finally, the development of methods of preparing hydrated calcium silicates has been directed toward a search for methods of manufacturing noncalcined cement. Such searches are based on the supposition that synthesized hydrated silicates after dehydration at comparatively low temperatures will not lose their ability to hydrate again.

The literature shows that two methods have been used for the preparation of hydrated calcium silicates: hydrothermal synthesis, and synthesis in which elevated pressures and temperatures are not used.

Among the earliest investigations devoted to the hydrothermal synthesis of hydrated calcium silicates was that of Daubrée [1] in which wollastonite was formed by heating calcium silicate glass with a small amount of water in a glass tube at 400°. Doelter [2] observed the formation of wollastonite from calcium bicarbonate and silica gel at 400-425°.

By heating a mixture of lime and amorphous silica with a small amount of calcium chloride at 470° for 48 hours, Schlapfer and Niggli [3] obtained hillebrandite $2CaO \cdot SiO_2 \cdot H_2O$. The heating was carried out in a silver crucible contained in a steel vessel. The authors observed the formation of hillebrandite at various ratios of calcium oxide to silica. There are no indications in the paper, however, of the yield of finished product.

In an investigation of the formation of hydrated calcium silicates from calcium oxide and finely ground quartz, Nagai [4] heated aqueous mixtures containing CaO and SiO_2 in the proportions 5:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:5 in nickel crucibles contained in an autoclave. Heating was carried out at temperatures in the range 133-212° for one to ten days. By the application of methods of chemical, microscopic, and in some cases, X-ray analysis, the author established that a six-day treatment in an autoclave of the most basic mixtures ($CaO:SiO_2 = 5:1$ and $3:1$) at 212° led to the formation of a product of composition $2CaO \cdot SiO_2 \cdot H_2O$, similar in its properties to artificial hillebrandite. At low temperatures, less basic mixtures gave a substance of composition $3CaO \cdot 2SiO_2 \cdot 3H_2O$ (afwillite), and at higher temperatures, $CaO \cdot SiO_2 \cdot 0.25 H_2O$ (xonotlite). The author gave also the results of a study of the reaction between calcium oxide and silica in a stream of superheated aqueous vapor mixed with air.

Vigfusson and coworkers [5] have synthesized hydrated calcium silicates by heating a mixture of calcium hydroxide with finely ground quartz sand in a platinum crucible in an autoclave at 170° in presence of a large excess of $Ca(OH)_2$. The hydrated silicate obtained, which had the composition $2.07 CaO \cdot SiO_2 \cdot 1.24 H_2O$, was compared with hydration products formed by the action of steam, in one case on cement mortar, and in another case pure dicalcium silicate. After removal of sand and lime from the cement mortar formed in this way, the sample had the composition $1.94 CaO \cdot SiO_2 \cdot 1.14 H_2O$. The X-ray photographs of these samples, like their optical properties, were similar to one another, but differed from those of natural hillebrandite. Repeat syntheses of hydrate calcium silicates in mixtures richer in lime ($CaO:SiO_2 = 4:1$) yielded a product which after removal of unchanged lime and silica had the composition $2.14 CaO \cdot SiO_2 \cdot 1.42 H_2O$ and gave an X-ray photograph differing from those of the previous samples. The authors established that the composition of the hydrated calcium silicate obtained depends not only on the conditions of synthesis, but also on the ratio $CaO:SiO_2$ in the mixture to be given the hydrothermal treatment.

Keevil and Thorwaldson [6] studied the action of saturated steam on tricalcium and β- and γ-dicalcium silicates, which were contained in platinum crucibles at 50 to 374°. Application of methods of chemical, microscopic, and X-ray analysis showed that after two weeks' treatment with steam at 170° both forms of dicalcium silicate gave identical crystalline products. Calcination of the hydrated dicalcium silicate gave β-$2CaO \cdot SiO_2$, not containing free lime. Treatment of tricalcium silicate with steam at 110° yielded the hydrated calcium silicate $2CaO \cdot SiO_2 \cdot H_2O$ and calcium hydroxide. At higher temperatures the authors observed the formation of fine-grain crystals of a material having refractions of Ng = 1.597 and Np = 1.589, no calcium hydroxide being eliminated. Characteristically, when this fine-grain material was dehydrated at 900°, free lime and β-dicalcium silicate were always formed.

In investigating the hydraulic properties of a clay-lime material that had been given a hydrothermal treatment, Budnikov [7] found that a hydrated silicate of composition $2CaO \cdot SiO_2 \cdot nH_2O$ was formed from kaolinite and calcium hydroxide roasted at 800-900°. According to this author's results, a hydrothermal treatment, particularly under pressure, considerably accelerates the process of forming $2CaO \cdot SiO_2 \cdot nH_2O$ and increases the strength of the product.

The review of the literature made by Steinour [8] concerning the system $CaO-SiO_2-H_2O$ shows that the synthesis of hydrated calcium silicates at ordinary temperatures and pressures is very difficult. It can be seen from this review that even in very recent papers very contradictory results are given. Thus some authors consider that, when silica gel and calcium hydroxide react under ordinary conditions, hydrated silicates of composition $CaO \cdot SiO_2 \cdot aq$, $3CaO \cdot 2SiO_2 \cdot aq$ and $2CaO \cdot SiO_2 \cdot aq$ are formed, the last compound being in equilibrium with a saturated solution of $Ca(OH)_2$. Other authors consider that only one compound of composition varying between $4CaO \cdot 5SiO_2 \cdot aq$ and $2CaO \cdot SiO_2 \cdot aq$ can exist in equilibrium with a saturated solution of calcium hydroxide.

As Mikhalchenko [9] showed, the rate of absorption of lime by silica at ordinary temperature and pressure depends to an appreciable extent on the degree of hydration of the silica. According to the author's results, more hydrated silica absorbs lime more readily than less hydrated silica does. The absorption of lime by silica is essentially a chemical process.

The investigation of the system $CaO-SiO_2-H_2O$ by Taylor [10] shows that the hydrated calcium silicates formed in the system are crystalline submicrogels, and it confirms the results of electron-microscope observations that revealed the crystalline nature of hydrated silicates. Taylor submitted hydrated calcium silicates obtained by three different methods to X-ray analysis and showed them to be identical. In spite of great care in carrying out the experiment, the author had great difficulty in obtaining reproducible results. The most recent investigations [11] give us reason to believe that the most probable cause of the poor reproducibility of results is the variation in dispersion of the silica particles.

This far from full review of the investigations shows that all the methods that have been applied for the synthesis of hydrated calcium silicates have given insignificant yields of ready products, have required a long time for the reaction in which the hydrated silicates are formed, and, what appears to be the most serious drawback, have demanded the introduction of a great excess of calcium hydroxide in order to yield hydrated silicates having a $CaO:SiO_2$ ratio of greater than unity.

EXPERIMENTAL

Synthesis of Hydrated Calcium Silicates

For the synthesis of hydrated calcium silicates we used the method of treating amorphous silica with a solution of calcium oxide. As Brauns [12] has pointed out, the method of preparing certain minerals by the action of solutions on solids was successfully applied already in the last century. The starting materials were calcium oxide obtained by the calcination of chemically pure calcium carbonate, and dehydrated amorphous silica. The calcination of calcium carbonate was carried out for one hour at 1000°, and the dehydration of amorphous silica for six hours at 500°. Chemical analysis showed that the CaO content of the calcined product was 99.71% and the SiO_2 content of the dehydrated amorphous silica was 99.80%.

Calcium oxide and amorphous silica taken in the necessary proportions were mixed in a porcelain mortar, and a small amount of glycerol dried at 160° was added immediately. The contents of the mortar were homogenized by prolonged grinding. The presence of glycerol during grinding was intended to prevent contact of the calcium

oxide and amorphous silica with atmospheric carbon dioxide and moisture. After the grinding, the mixture was transferred to a 250 ml conical flask, into which sufficient glycerol was added to make its total amount up to 8-9 times the weight of the dry charge. The conical flask was then placed on an electric hotplate covered with a thin sheet of asbestos and was heated with continuous stirring at 180-185°. When this temperature was reached, the mixture began to froth. Froth formation was reduced by cutting down the supply of heat and shaking the flask; it stopped 3-3.5 hours after the attainment of the temperature of 180°, and the liquid in the flask became clear. Complete dissolution was an indication that the reaction leading to the formation of calcium silicate was complete. Heating was discontinued, and the contents of the flask were cooled to ordinary temperature and diluted with distilled water, when a white precipitate of hydrated calcium silicate came down. After twelve decantations, the precipitate was pressed off on a vacuum funnel, washed, first with distilled water and then with alcohol, and then dried for four hours at 100°. Precipitation of hydrated calcium silicate must be carried out only from cold solution, because the precipitate obtained by dilution of a hot solution settles slowly, and decantation is very prolonged.

When the mixture is heated, calcium oxide dissolves first with formation of calcium "glycerate":
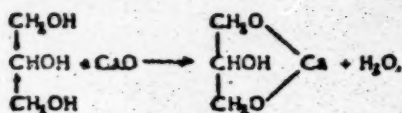
and the glycerate reacts with silica with formation of calcium silicate:
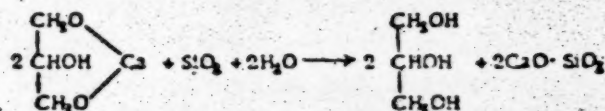
On dilution of the cold solution and washing the precipitate, the hydrated silicate is formed:

$$2CaO \cdot SiO_2 + H_2O \longrightarrow 2CaO \cdot SiO_2 \cdot H_2O.$$

It was shown by heating a mixture of glycerol and dehydrated amorphous silica under these conditions that silicon dioxide is insoluble in pure glycerol. We may therefore consider that the dissolution of amorphous silica is the result of its reaction with calcium glycerate.

It should be noted that in the hydration process more than one molecule of water unites with one molecule of dicalcium silicate. However, drying of the hydrated product at 100° to constant weight followed by chemical analysis of the hydrated silicate obtained shows that one molecule of water is held fairly firmly.

For the synthesis of hydrated dicalcium silicate $2CaO \cdot SiO_2 \cdot H_2O$, which is of the greatest practical interest and which is prepared under hydrothermal conditions with the greatest experimental difficulties, we prepared the following charge:

Calcium oxide .... 4.21 g
Amorphous silica .... 2.25 g
Glycerol .... 60.00 g

In the whole series of experiments the product from the drying of the pressed and washed precipitate was a white stonelike material, readily ground in a mortar. An attempt to use the fraction of finely ground rock crystal* passing through a sieve having 10,000 mesh per cm² did not give positive results. In this case the reaction of silicate formation proceeded very slowly, and the use of rock crystal, instead of amorphous silica was found to be inexpedient.

Investigation of the Products of the Synthesis

Chemical analysis of the hydrated silicate dried at 100° showed that the synthetic product was identical in composition with hydrated dicalcium silicate (Table 1).

The synthesized hydrated silicate could not be studied microscopically even at the greatest magnification, the particles being evidently so small that they appeared amorphous. X-ray investigation, however, showed that

* The X-ray photograph was taken by Yu. G. Sokolov.

TABLE 1

Found in synthesized sample (%)				Calculated for 2CaO·SiO₂·H₂O (%)			
CaO	SiO₂	H₂O	Total	CaO	SiO₂	H₂O	Total
58.56	31.44	9.83	99.83	58.97	31.57	9.46	100.0

TABLE 2

Taylor's results		Found for 2CaO·SiO₂·H₂O	
d/n	I/I₁	d/n	I/I₁
10.00	weak		
3.05	strong	3.053	10
2.80	strong	2.809	6
2.40	weak	2.412	2
2.20	very weak	2.211	1
2.10	very weak	2.109	1
2.00	medium	2.014	6
1.80	strong	1.810	9
1.55	weak	1.561	3
1.39	very weak	1.401	1
1.225	very weak	1.232	1
1.165	very weak	1.170	1
1.100	extremely weak		
1.045	extremely weak		

the hydrated silicate obtained had a crystalline character (X-ray photograph in cylindrical camera with K$_\alpha$Co rays). Also, calculations from the X-ray photograph and comparison of the results of the calculations with those of Taylor [10] for samples of hydrated calcium silicate synthesized from tricalcium silicate and containing CaO: SiO₂ in the ratio 1.94:1, showed that the structures of the two materials were of the same type (Table 2).

Microscopic investigation of the hydrated silicate after being dehydrated by a two-hour calcination at 900° showed that it consisted of fine granular aggregates having the refraction values Ng = 1.734 and Np = 1.718. Calcination at the same temperature for four hours encouraged the growth of the grains of dicalcium silicate, without changing the values of the refractive indices. There was no free lime in the dehydrated preparation.

SUMMARY

1. Calcium "glycerate" reacts with amorphous silica with formation of dicalcium silicate, readily isolable from the glycerol solution by dilution, when it is obtained in the form of a hydrated silicate of composition 2CaO·SiO₂·H₂O.

2. The proposed method permits the preparation of dicalcium silicate without the introduction of excess of calcium oxide into the reaction mixture. The reaction

between calcium glycerate and silica gives a 100 % yield of dicalcium silicate. The hydrated calcium silicate obtained is a crystalline compound.

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SYNTHESIS OF 5-ALKYL-1,3,4-OXADIAZOL-2(3H)-ONES AND STUDY OF THEIR REACTIONS WITH AMMONIA

V. M. Rodionov and V. K. Zvorykina

In one of our previous communications [1] it was shown that, when Hofmann's reaction is carried out with amides of certain N-acylated β-aryl-β-amino acids, the final products include 5-substituted 1,3,4-oxadiazol-2(3H)-ones (I):
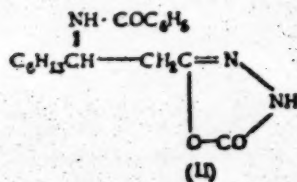
$$Ar-C=N$$
$$O-CO \quad HN$$
(I)
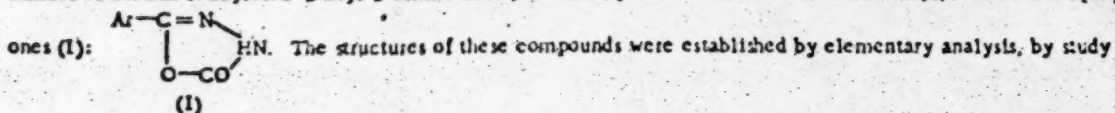
The structures of these compounds were established by elementary analysis, by study of their properties and reactions, and also by confirmatory synthesis by Lieser and Nischk's elegant method [2]:

$$ArCONH-NH_2 \xrightarrow{COCl_2} Ar-C=N$$
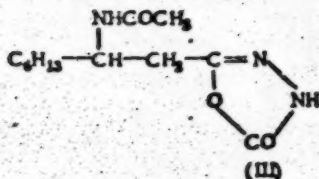$$O \quad NH$$
$$CO$$
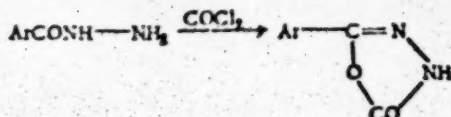
The study of oxadiazolone derivatives is of interest on its own account, and a more detailed investigation was therefore made of these compounds. The first experiments were carried out on 3-aminononanoic acid, which has already been well studied by us. As starting materials for the synthesis of these substances we prepared the hydrazides of the N-benzoyl and N-acetyl derivatives of 3-aminononanoic acid by heating their esters with hydrazine hydrate.

The hydrazides obtained were converted by a somewhat modified form of Lieser and Nischk's method (see Experimental) into 5-(2-benzamidooctyl)-1,3,4-oxadiazol-2(3H)-one (II) and 5-(2-acetamidooctyl)-1,3,4-oxadiazol-2(3H)-one (III):

$$NH \cdot COC_6H_5$$
$$C_6H_{13}CH-CH_2C=N$$
$$NH$$
$$O-CO$$
(II)

and

$$NHCOCH_3$$
$$C_6H_{13}-CH-CH_2-C=N$$
$$NH$$
$$O \quad CO$$
(III)

A number of interesting observations were made when attempts were made to convert the hydrazides of β-amino acids into semicarbazides by treatment with potassium cyanate. Thus the hydrazide of 3-acetamidononanoic acid reacts fairly smoothly (66% yield) with KCNO, giving the corresponding semicarbazide derivative (IV):

$$NH \cdot COCH_3$$
$$C_6H_{13}CH-CH_2CO-NHNH \cdot CONH_2$$
(IV)
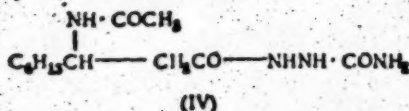
In the analogous reaction with the hydrazide of 3-benzamidononanoic acid, a substance of acidic nature, m.p. 166°, was isolated; its structure has not yet been established.

Treatment of the hydrazide of heptanoic acid with potassium cyanate yielded two compounds: one of a neutral character, m.p. 173°, corresponding in analysis to 1-heptanoylsemicarbazide $C_6H_{13}CONHNHCONH_2$, and a second of an acidic character, m.p. 167°. The latter substance corresponded in elementary analysis to the semicarbazide derivative + one molecule of water. A mixed test of the two did not give a depressed melting point (sharp melting at 173°). It was later found that the products are mutually interconvertible. Thus, when the substance of m.p. 167° is submitted to a long drying process (at a temperature of not above 100°), it loses the ability to dissolve in alkalis and is converted into 1-heptanoylsemicarbazide. On the other hand, the latter, on being recrystallized from water, melts, after drying in a desiccator, at 167°, acquires acid properties, and dissolves in alkalis. The mechanism of the mutual conversion of these compounds has not yet been established.

When the semicarbazide derivative is heated with a 10% solution of caustic potash, it loses one molecule of water, yielding 5-hexyl-1H-1,2,4-triazol-3(2H)-one [2]:
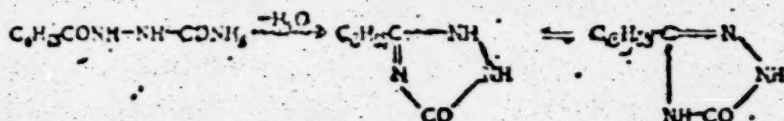

In the chemical literature there are differences in interpretation with respect to the structures of certain triazolones. Thus, Girard [3] considers that the triazolone compounds obtained by oxidation of semi-carbazones of α-keto acids with iodine have the oxo structure; on being heated with alkalis they pass into hydroxy compounds. Compounds of the two types have sharp melting points and different properties. Unlike Girard, Gehlen [4] asserts that in this reaction cyanhydrazides are formed, and he proves this by synthesizing several of these compounds by the action of cyanogen bromide on hydrazides.

In connection with this conflict of evidence it was of interest to determine whether it is possible to convert oxadiazole compounds into triazole derivatives by treatment with ammonia. It is well known that certain 1,3-oxazine and γ-pyrone compounds fairly readily exchange O for NH. Such an attempt was made with 5-substituted 1,3,4-oxadiazol-2(3H)-ones, and it was found that, when 5-hexyl-1,3,4-oxadiazol-2(3H)-one is heated with alcoholic ammonia under a moderate pressure, scission of the five-membered ring occurs, and 1-heptanoylsemicarbazide is formed.
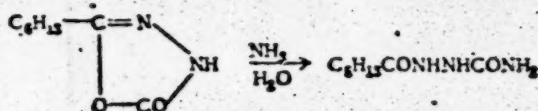
Extension of this reaction to 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one [2] led to the isolation of two substances: 3-ureidononanoic acid and 3-(3-aminoureido)nonanoic acid:
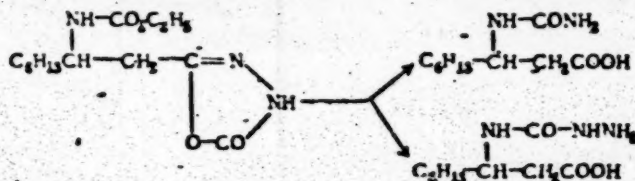
The unexpected formation of these compounds, especially the second, could be explained only by the intermediate formation of a hexahydropyrimidine ring and its subsequent hydrolysis, in a manner similar to that of the reaction that we have studied [5], in which amides of N-carboxycarbonyl derivatives of β-amino acids are converted into β-ureido acids according to the following equations:
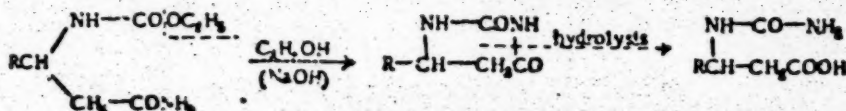
A similar explanation may be proposed also for the formation of 3-(3-aminoureido)nonanoic acid by the reaction of ammonia with 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one. In this case the reaction mechanism is somewhat more complex and may be presented in two ways:
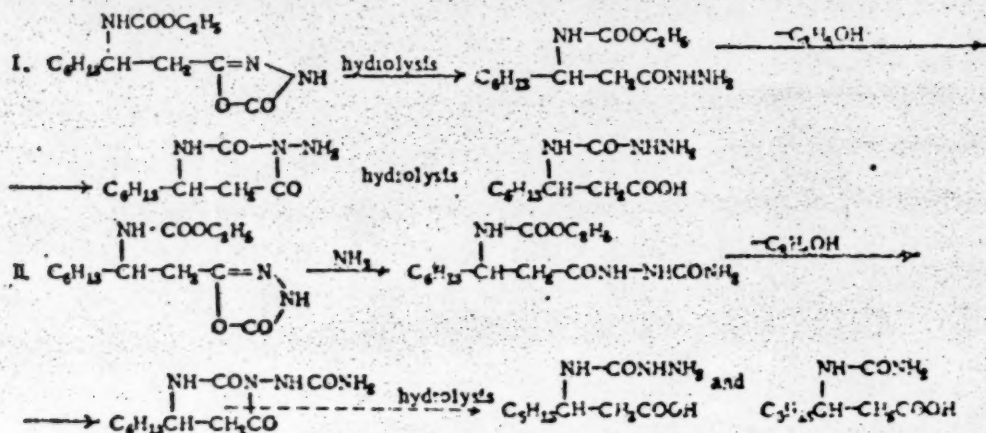
In both cases a hexahydropyrimidine derivative is formed intermediately, and it is then split up with formation of the β-(3-aminoureido) acid. The latter compound is of an amphoteric nature, dissolving both in dilute mineral acids and in alkalis; it is readily soluble in hot water, poorly soluble in cold water, and insoluble in organic solvents.

EXPERIMENTAL

Preparation of 5-(2-Benzamidooctyl)-1,3,4-oxadiazol-2(3H)-one

The hydrazide of 3-benzamidononanoic acid was prepared by heating an alcoholic solution of the ethyl ether of 3-benzamidononanoic acid for 36 hours with three times its amount of hydrazine hydrate; it crystallized from aqueous alcohol in colorless needles, m.p. 156-157° (yield 81%). The hydrazide of 3-benzamidononanoic acid (2 g) was heated in an oil bath for one hour at 120° and two hours at 150° with 40 ml of a 10% solution of $COCl_2$ in toluene. The excess of toluene and $COCl_2$ was driven off under a vacuum. The residue (1.69 g, 77%), a hard white mass, was recrystallized from aqueous alcohol, yielding fine colorless prisms, m.p. 126°.

Found %: C 63.95; 62.83; H 6.73; 6.84; N 13.72; 13.71
$C_{17}H_{23}O_3N_3$. Calculated %: C 64.35; H 7.25; N 13.25

Preparation of 5-(2-Acetamidooctyl)-1,3,4-oxadiazol-2(3H)-one

The hydrazide was prepared by heating 3-acetamidononanoic acid in alcoholic solution for 36 hours with three times its amount of hydrazine hydrate; colorless needles (from water), m.p. 165°, yield 64%. The hydrazide of 3-acetamidononanoic acid (2 g) was heated in an oil bath with 40 ml of a 10% solution of $COCl_2$ in toluene; one hour at 120°, and two hours at 150°. The excess $COCl_2$ and toluene were driven off under a vacuum. The solid product obtained was treated with 10% KOH, the alkaline solution was extracted with ether, the extract was filtered from some foreign matter, and it was then acidified with HCl. The white crystalline precipitate that formed was filtered off, washed with water, and recrystallized from water (1.72 g, 73.5%): long colorless needles, m.p. 116°.

Found %: C 56.95; 57.19; H 8.35; 8.57; N 16.90; 16.97
$C_{12}H_{21}O_3N_3$. Calculated %: C 56.6; H 8.2; N 16.5

Preparation of 5-Hexyl-1,3,4-oxadiazol-2(3H)-one from the Hydrazide of Heptanoic Acid.

The hydrazide was prepared by heating ethyl heptanoate in alcoholic solution for 36 hours with a three-fold excess of hydrazine hydrate. It crystallized from water as colorless needles, m.p. 62°.

Found %: N 19.57; 19.70
$C_7H_{16}ON_2$. Calculated %: N 19.44

The hydrazide of heptanoic acid (1.3 g) was heated for two hours at 120-150° with 60 ml of a 10% solution of COCl₂ in toluene. The excess of COCl₂ and toluene were driven off under a vacuum, and the residue was distilled at 24 mm, yielding 1 g (65%) of a liquid of b.p. 192-196°. A second fractionation yielded a fraction of b.p. 193-195°/24 mm. The 5-hexyl-1,3,4-oxadiazol-2(3H)-one previously obtained by Hofmann's reaction boiled at 184-186°/18 mm.

Hydrolysis of 5-Hexyl-1,3,4-oxadiazol-2(3H)-one

When the oxadiazolone was boiled for three days with water over a gauze, a white crystalline substance, m.p. 81-82°, was precipitated. When admixed with the hydrazide of heptanoic acid, there was no depression in melting point.
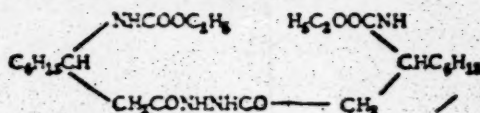
Preparation of the Hydrazide of 3-(Ethoxycarbonylamino)-nonanoic Acid

1. Preparation of the hydrazide from the ethyl ester of 3-(ethoxycarbonylamino)nonanoic acid. The ester (1 g) in alcoholic solution was heated for 15 hours with three times the amount of hydrazine hydrate. After distilling two-thirds of the alcohol off, we crystallized the precipitate from water and obtained 0.85 g (about 90%) of product, m.p. 142°.

Found %: N 16.46; 16.61
C₂H₂₁O₃N₃ Calculated %: N 16.21

2. Preparation of the hydrazide from the acid chloride by adding the latter in ethereal solution to a three-fold excess of hydrazine hydrate. The product was the diacylhydrazine:

$$C_4H_{13}CH \overset{NHCOOC_2H_5}{\underset{CH_2CONHNHCO}{}} \quad \overset{H_5C_2OOCNH}{\underset{CH_2}{}} CHC_6H_{13}$$

Melting point after recrystallization from alcohol: 212°.

Found %: N 11.70 and 11.78
C₂₄H₄₆O₆N₄ Calculated %: N 11.52

Preparation of 5-[2-(Ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one from the Hydrazide

The hydrazide (0.8 g) was heated for 1.5 hours at 120-150° in an oil bath with a four-fold excess of a 10% solution of COCl₂ in toluene. The toluene was distilled off under vacuum, and the residue was treated with 10% NaOH. Acidification yielded a solution of 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one (0.7 g, 80%), m.p. 71-72°. In admixture with a sample (m.p. 73°) obtained by Hofmann's reaction, it melted at 72-73°.

Hydrolysis of 5-[2-(Ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one

A 20-hour boiling with water over a gauze yielded a precipitate from which a substance of m.p. 140-142° was isolated [in admixture with the hydrazide of 3-(ethoxycarbonylamino)nonanoic acid (m.p. 142°) it melted at 142°]. There was also a very small amount of a substance of m.p. 160°; in admixture with the amide of 3-(ethoxycarbonylamino)nonanoic acid it melted at 135-143°.

Preparation of the Ureide of 3-(Ethoxycarbonylamino)nonanoic Acid

The acid chloride obtained by heating 6.2 g of 3-(ethoxycarbonylamino)nonanoic acid with the theoretical amount of SOCl₂ at 40° was dissolved in 30 ml of absolute ether and added dropwise with cooling to double the amount of urea as a suspension in absolute ether. When the whole of the acid chloride had been added, the solution was stirred for a further two hours; the ether was driven off, and the residue remaining in the flask was heated in a boiling water bath for six hours. The product obtained was washed several times with ether, with 5% NaOH, and with water, and was recrystallized from 300 ml of alcohol. The ureide came down in the form of fine colorless needles, m.p. 198° (6 g, 60%).

Found %: N 14.80; 14.98
C₁₃H₂₅O₄N₃ Calculated %: N 14.63

The Action of Hypobromite on the Ureide of 3-(Ethoxycarbonylamino)nonanoic Acid

The ureide (5 g) was added under stirring over a period of two hours to a solution of hypobromite prepared at −5–10° from 1 ml of bromine in 30 ml of 10% NaOH. When solution was complete, the liquid was stirred for a further two hours, after which it was heated to 80° and cooled. On addition of HCl to a weakly alkaline reaction, an oil was precipitated. This crystallized out on the next day in clear colorless plates, m.p. 73°. In admixture with 3-(ethoxycarbonylamino)nonanoic acid (m.p. 79–80°) it melted at 60–62°. On further acidification to a weakly acid reaction, an oil was precipitated, from which, by treatment with bicarbonate, 3-(ethoxycarbonylamino)nonanoic acid was isolated together with some of the first substance, m.p. 73°. Further acidification yielded a precipitate of 3-(ethoxycarbonylamino)nonanoic acid. The products were: substance of m.p. 73° (1.82 g, 42%), which was 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one, and 3-(ethoxycarbonylamino)nonanoic acid (2.18 g, 43.6%).

Analysis of substance, m.p. 73°:

Found %: C 54.77, 54.99, H 8.38; 8.33; N 14.22; 14.29

$C_{13}H_{23}O_4N_2$ Calculated %: C 54.73; H 8.47; N 14.73

Preparation of 1-(3-Acetamidononanoyl)semicarbazide

KCNO (1 g) was added to 2 g of the hydrazide in 50 ml of water + 1 ml of concentrated HCl, and the solution was heated for two hours over a gauze. When the solution was cooled, a precipitate appeared, and this was filtered off, the filtrate being then evaporated down to low volume and again filtered. Altogether, 1.56 g (66%) of a substance giving melting points of 205° and 202° was obtained. After being recrystallized from water it was obtained as colorless plates, m.p. 212°.

Found %: C 53.03; 52.93; H 9.25; 9.20; N 20.5; 20.13

$C_{12}H_{24}O_3N_4$ Calculated %: C 52.9; H 8.82; N 20.51

Preparation of 1-Heptanoylsemicarbazide

KCNO (5.5 g) was added with cooling to a solution of 6 g of the hydrazide of heptanoic acid in 25 ml of water + 6.5 ml of 33% HCl. When the reaction mixture was heated, the precipitate that formed on addition of the cyanate went into solution; reprecipitation occurred when the solution was cooled. The precipitate was treated with 5% NaOH solution, and a part of it went into solution. When the alkaline solution was acidified, a white crystalline precipitate (0.2 g) separated; it was recrystallized from water and was found to melt at 167°. The alkali-insoluble part of the reaction product was also recrystallized from water and dried in a drying cabinet at 100°, yielding 5.7 g of fine needles melting at 173°. The first substance (m.p. 167°) was readily soluble in alkali and was precipitated from alkaline solution by acid; the second was insoluble. There was no depression in a mixed melting point (173°). The substance of m.p. 173° after being recrystallized from water and dried in a desiccator was found to melt at 167° and to acquire the ability to dissolve in alkalis, whereas the substance of m.p. 167° after long drying at 100° was found to melt at 173° and to have lost the ability to dissolve in alkalis.

Analysis of the substance of m.p. 173°:

Found %: C 51.59; 51.97; H 9.42; 9.26; N 22.58; 22.75

$C_8H_{17}O_2N_3$ Calculated %: C 51.33; H 9.09; N 22.46

Analysis of the substance of m.p. 167°:

Found %: C 46.08; 46.25; H 9.72; 9.60; N 20.34; 20.27

$C_8H_{17}O_2N_3 \cdot H_2O$. Calculated %: C 46.83; H 9.27; N 20.48

Preparation of 5-Hexyl-1H-1,2,4-triazol-3(2H)-one from 1-Heptanoylsemicarbazide

1-Heptanoylsemicarbazide (4.2 g) was heated at the boil over a gauze with 40 ml of 10% KOH. After 1 hour 30 minutes the solid present went into solution and did not separate when the solution was cooled. On acidification with HCl colorless needles (3.35 g) were precipitated. The melting point after recrystallization from water (300 ml) was 168.5°. It was readily soluble in caustic alkalis, being reprecipitated from solution by acid; it was insoluble in a solution of sodium carbonate or bicarbonate. In admixture with the substance of m.p. 167° from the preceding experiment it melted at 151–154°.

Found %: C 56.07; 56.87; H 8.74; 8.63; N 25.05; 25.17

$C_8H_{15}ON_3$. Calculated %: C 56.80; H 8.85; N 24.85

Action of Alcoholic Ammonia on 5-Hexyl-1,3,4-Oxadiazol-2(3H)-one

The hexyloxadiazolone (0.3 g) was heated in a sealed tube for three hours with 15 ml of an 8% alcoholic solution of NH_3. The alcohol was driven off, leaving a white crystalline substance. It melted, after recrystallization from water and drying on a water bath, at 171°. In admixture with 1-heptanoylsemicarbazide (m.p. 173°) it melted at 171-172°.

Action of Alcoholic Ammonia on 5-(2-Acetamidooctyl)-1,3-4-oxadiazol-2(3H)-one

The oxadiazolone derivative (0.5 g) was heated in a sealed tube for four hours at 120° and then 30 minutes at 140° with an 8% alcoholic solution of NH_3. The alcohol was distilled off, and the residue was dissolved in hot water. The solution was filtered from foreign matter and evaporated down, yielding a white crystalline substance of m.p. 160-180°. When this was treated with alcohol, a part went into solution. The residue melted, after being recrystallized from water, at 211°. In admixture with the previously obtained semicarbazide derivative (m.p. 212°) it melted at 211°. After removal of the alcohol by distillation and recrystallization of the residue from water, a hydrazide of m.p. 163° was obtained. In admixture with the previously prepared hydrazide of m.p. 165° it melted at 165°.

Action of Alcoholic Ammonia on 5-[2-(Ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one

5-[2-(Ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one (0.5 g) was heated for three hours at 120° in a sealed tube with an 8% alcoholic solution of NH_3. After removal of alcohol by distillation, a crystalline substance of m.p. 117-120° remained. When this was recrystallized from water, two substances were obtained: one melting at 127-128°, and the other at 133-135°.

All the properties of the first compound, including its melting point, coincided with those of the 3-ureido-nonanoic acid previously prepared by us (in admixture, the two samples melted at 128°). The second compound was of an amphoteric character, being readily soluble in dilute mineral acids and caustic alkalis. After a double wash with ether and recrystallization from water, the melting point rose to 145° (with decomposition). In accordance with the elementary analysis of this compound we suggested that it was 3-(3-aminoureido)nonanoic acid, and this suggestion was confirmed by all further investigation. 3-(3-Aminoureido)nonanoic acid is readily soluble in hot water (colorless rhombic plates, sticking together by the side faces) and in alcohol. It is insoluble in ether and in benzene.

Found %: C 51.60; 51.41; H 9.00; 9.13; N 18.16; 18.33
$C_{12}H_{24}O_3N_3$ Calculated %: C 51.95; H 9.09; N 18.18

SUMMARY

1. The syntheses are given of several 5-alkylated derivatives of 1,3,4-oxadiazol-2(3H)-one, namely 5-(2-benzamidooctyl)-, 5-(2-acetamidooctyl)-, 5-hexyl-, and 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one.

2. It has been shown that, when 5-substituted 1,3,4-oxadiazol-2(3H)-ones are hydrolyzed, hydrazides of the original β-amino acids are formed.

3. It has been found that, when subjected to Hofmann's reaction, the ureide of 3-(ethoxycarbonylamino)-nonanoic acid also gives 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one.

4. The action of alcoholic ammonia on 5-substituted 1,3,4-oxadiazol-2(3H)-ones has been studied, and it has been found that in this reaction 5-hexyl- and 5-(2-acetamidooctyl)-1,3,4-oxadiazol-2(3H)-ones form 1-acylsemicarbazides derived from the corresponding β-amino acids.

5. When 5-[2-(ethoxycarbonylamino)octyl]-1,3,4-oxadiazol-2(3H)-one is heated with alcoholic ammonia, it gives a mixture of 3-ureido- and 3-(3-aminoureido)-nonanoic acids. The mechanism of this reaction has been elucidated.

6. A study has been made of methods of preparing 1-(3-acetamidononanoyl)- and 1-heptanoyl-semicarbazides.

7. 1-Heptanoylsemicarbazide has been converted into 5-hexyl-1H-1,2,4-triazol-3(2H)-one.

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SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XVI. CONDENSATION OF 2-METHYL-2-CYCLOHEXEN-1-ONE WITH 2-METHOXY-1,3-BUTADIENE. SYNTHESIS OF 3,4,4a,7,8,8a-HEXAHYDRO-4a-METHYL-6-VINYL-2(1H)-NAPHTHALENONE AND 3,4,4a,5,6,8a-HEXAHYDRO-8a-METHYL-6-VINYL-2(1H)-NAPHTHALENONE

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S. N. Ananchenko, and V. M. Andreev

In a previous communication [1] from our laboratory, we described the condensation of 2-methoxy-1,3-butadiene (I) with 2-methyl-2-cyclohexen-1-one (II). From the product, the hexahydromethoxymethyl-1(2H)-naphthalenone (III), we obtained some bicyclic alcohols (IV, V, and VI) and the hexahydromethylvinyl-2(1H)-naphthalenone (VII), which are important intermediate products for the synthesis of steroid compounds and related substances:
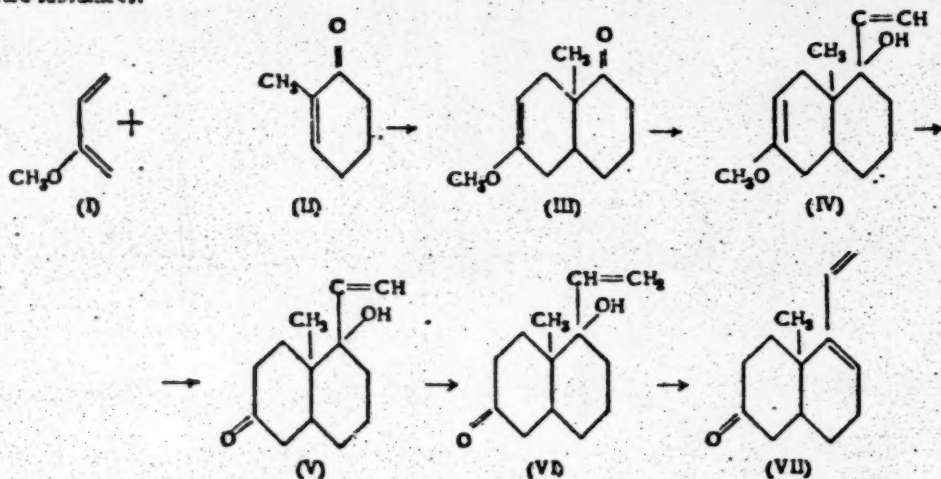

Condensation of the dienone (VII) with various dienophiles permitted the preparation of various polycyclic compounds, including, in particular, steroid tetracyclic diketone, having hydrogenated cyclopentaphenanthrene and chrysene skeletons and containing angular methyl groups. Not all of these intermediate products, however, were prepared sufficiently smoothly and in satisfactory yield. In the present investigation, therefore, we have undertaken a detailed study of all stages of the preparation of the dienone (VII), and also of the possibility of improving the yields of all compounds required for its synthesis.

First of all, improvement was made in the method of preparing 2-methoxy-1,3-butadiene (I). It was found that consistent yields (75-80 %) of this diene were obtained by the splitting of methanol from 1,3,3-trimethoxybutane, not by means of freshly calcined potassium hydrogen sulfate, as recommended by Dikstra [2], but by the use of the residue from a previous experiment, containing potassium hydrogen sulfate mixed with organic substances. By this means it was found possible to obtain 2-methoxy-1,3-butadiene in a yield of 75-80%, instead of the 60-65% obtained by Dikstra's procedure.

A method was developed in detail also for the preparation of 2-methyl-2-cyclohexen-1-one (II) by the bromination of 2-methylcyclohexanone, as described in one of our communications. In the study of the

condensation of 2-methoxy-1,3-butadiene (I) with 2-methyl-2-cyclohexen-1-one (II), the time and temperature of the reaction and the ratio of the components were varied. The best results were obtained with an eight-fold excess of the methylcyclohexenone at a temperature of 260-270° and condensation time of 2.5 hours. It was established also that additions of diethylaniline have a favorable influence. Under these conditions the yield of the hexahydromethoxymethyl-1(2H)-naphthalone (III) was 45-60%, reckoned on the methylcyclohexenone, and 27-29%, reckoned on the methoxybutadiene.

It was found that the condensation reaction goes in both of the theoretically possible directions, so that together with 2,3,4a,5,8,8a-hexahydro-6-methoxy-8a-methyl-1(2H)-naphthalenone (III), appreciable amounts (about 15%) are formed also of 2,3,4a,5,8,8a-hexahydro-7-methoxy-8a-methyl-1(2H)-naphthalone (IIIa):
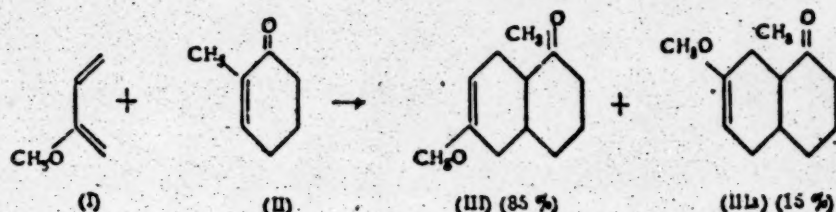
Owing to the closeness of their boiling points, it was not found possible to separate the isomers (III) and (IIIa), but the acetylenic hydroxy ketones (V) and (Va) prepared from them were readily separated by fractional crystallization.
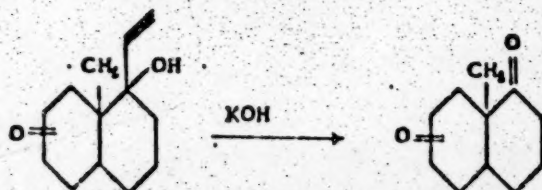
Condensation of the mixture of (III) and (IIIa) with sodium acetylide in liquid ammonia yielded a mixture of isomeric acetylenic methoxy alcohols (IV) and (IVa), from which only 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6-methoxy-8a-methyl-1-naphthol (IV) could be isolated in the crystalline form. It was later found convenient not to separate the methoxy alcohols (IV) and (IVa) in the pure state, but to convert them by the action of 1% hydrochloric acid into the hydroxy ketones (V) and (Va). From the mixture of (V) and (Va) it was found possible by fractional crystallization to isolate pure 5-ethynyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (V) in 40-46% yield, calculated on the ethynyloctahydromethoxymethylnaphthol taken. It was more difficult to isolate 8-ethynyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone (Va), which was obtained in 7-9% yield.
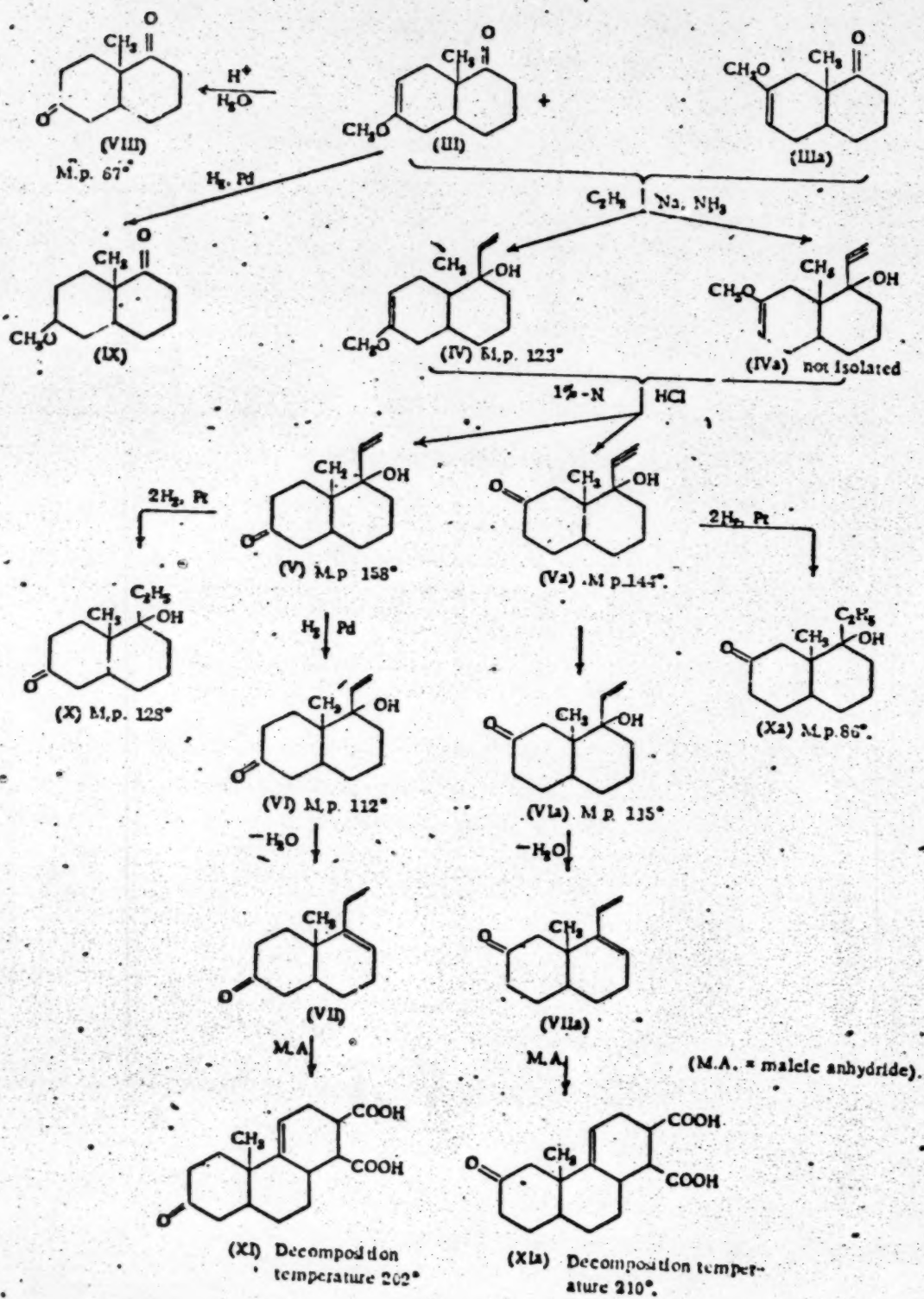
Distillation of the mother liquors yielded 15-20% of a liquid mixture of the hydroxy ketones (V) and (Va) and also, evidently of their isomers, differing in the spatial arrangement of the substituents in position 1 with respect to the angular methyl group.

Exhaustive hydrogenation of the acetylenic hydroxy ketones (V) and (Va) gave the corresponding saturated hydroxy ketones (X) and (Xa). Selective hydrogenation of the acetylenic hydroxy ketones (V) and (Va) over a Pd catalyst gave the crystalline vinyl hydroxy ketones (VI) and (VIa). Dehydration of the latter with the aid of potassium hydrogen sulfate yielded the dienones (VII) and (VIIa). It should be noted that in the dehydration the conditions given in the Experimental part must be strictly observed, as otherwise not only does the yield fall, but the dienone itself becomes less active, possibly owing to transposition of double bonds.

The dienones (VII) and (VIIa) react in the cold with maleic anhydride, giving the corresponding condensation products. The reaction was complicated, however, by the formation of polymeric compounds, so that the yield of the acids (XI) and (XIa) was only about 10%. (See page 71).

The obtaining of two series of isomers made it necessary to prove their structures, which has been done previously for the hexahydromethoxymethyl-1(2H)-naphthalenone (III) on the basis of model examples and analogies from the literature. It was at first proposed to convert each of the acetylenic hydroxy ketones (V) and (Va) into the corresponding diketones by the action of caustic potash according to the reaction:

(VIII) M.p. 67°

(III)

(IIIa)

H⁺ / H₂O

H₂, Pd

C₂H₂ | Na, NH₃

(IX)

(IV) M.p. 123°

(IVa) not isolated

1% - N HCl

2H₂, Pt

(V) M.p. 158°

(Va) M.p. 145°.

2H₂, Pt

(X) M.p. 128°

H₂ Pd

(VI) M.p. 112°

(VIa) M.p. 115°

(Xa) M.p. 86°.

−H₂O

−H₂O

(VII)

(VIIa)

M.A

M.A

(M.A. = maleic anhydride).

(XI) Decomposition temperature 202°

(XIa) Decomposition temperature 210°.

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The diketones formed could be related by a series of reactions to well-known naphthalene hydrocarbons. Attempts at splitting the acetylenic hydroxy ketone by the action of caustic potash under various conditions did not, however, give a positive result; the hydroxy ketone was resinified, and the yield of diketone was negligible. Another method of proving the structure was therefore chosen; it may be represented by the scheme:
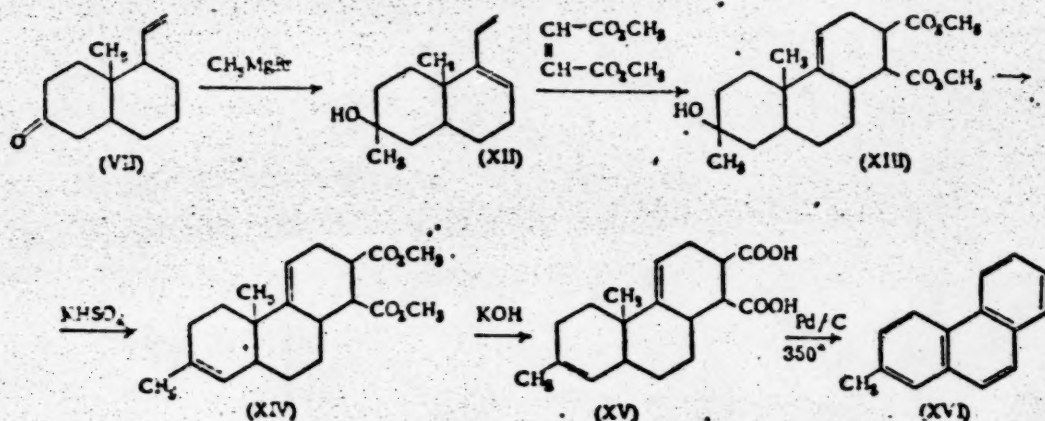
The diketone (VII) reacted with methylmagnesium bromide, giving a 90% yield of 1,2,3,4,4a,7,8,8a-octahydro-2,4a-dimethyl-5-vinyl-2-naphthol (XII). Condensation of the latter with dimethyl maleate yielded the dicarboxylic ester (XIII), which without being isolated, was dehydrated to give the dimethyl ester (XIV) of the dehydro-methylphenanthrenecarboxylic acid (XV). Hydrolysis gave the free acid (XV), which was dehydrogenated over palladium, giving 2-methylphenanthrene (XVI). The melting points of 2-methylphenanthrene itself and of its picrate coincided with the data given in the literature, as will be seen from Table 1.

TABLE 1

Substance	M.p. of hydrocarbon (°C)	M.p. of picrate (°C)
2-Methylphenanthrene (data in literature [3])	57-58	118-119
2-Methylphenanthrene (our results)	57-58.5	115-117
3-Methylphenanthrene (data in literature [4])	63	137-138

TABLE 2

Substance	M.p. of hydrocarbon (°C)	M.p. of picrate (°C)
2-Methylchrysene (data in literature [5])	229-230	143-146
2-Methylchrysene (our results)	222-223	145.5-146
3-Methylchrysene (data in literature [6])	170	164
3-Methylchrysene (our results)	166-169	160-161

The same procedure for proof of structure was applied also to the hydroxy ketone (Va), but it did not yield definite results, since the final products, in particular 3-methylphenanthrene, could not be isolated in a pure form. It was however, important to find a method of proving the structure that would be applicable to both isomers and would thus give comparable results. The following series of reactions, in which we successfully related the hydroxy ketones (V) and (Va) to known chrysene homologs, were therefore undertaken.

Dehydration of the dienols (XII) and (XIIa) with potassium hydrogen sulfate yielded the trienes (XVII) and (XVIIa), and condensation of these with 2-cyclohexen-1-one yielded the ketones (XVIII) and (XVIIIa) (in impure form). These substances were reduced by Kizhner's method, and dehydrogenation of the products gave 2-methylchrysene (XX) and 3-methylchrysene (XXa). The melting points of these hydrocarbons and of their picrates were in accord with data in the literature, as will be seen from Table 2.
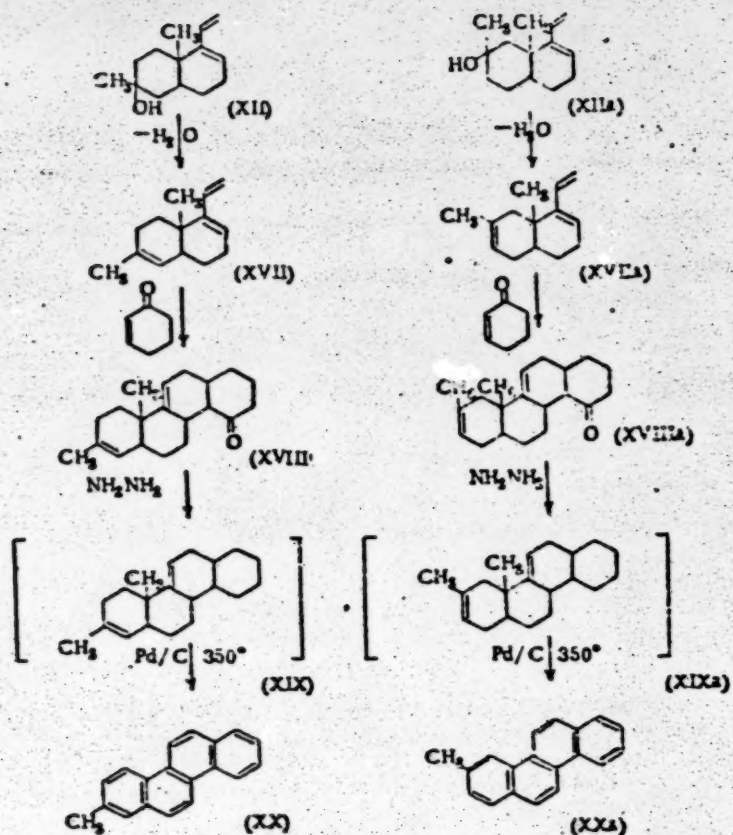
The structures of the dienones (VII) and (VIIa) and of all the associated compounds have therefore been rigorously proved.

The fact that in the diene condensation appreciable amounts (about 15%) of the 7-methoxy compound (IIIa) (meta isomer) were formed in addition to the 6-methoxy compound (III) (para isomer) deserves special attention. In the condensation of a 2-substituted butadiene with an unsymmetrical dienophile, two isomers may theoretically be formed:
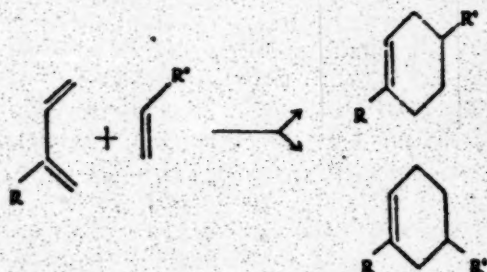
Actually, Aschan [7] found, as long ago as 1923, that isoprene, when dimerizing, yields not only dipentene, but also the meta-isomer, diprene. Quite recently, Alder and Vogt [8] have shown that, when isoprene condenses with 3-buten-2-one or methyl acrylate, appreciable amounts (up to 15%) of meta-isomer are formed. In reactions, however, with 2-substituted butadienes having electronegative substituents (Cl, CN, OR, etc.), only para isomers have been isolated. Precisely similar results were obtained in the dimerization of chloroprene [9], 2-cyanobutadiene [10], 2-phenylbutadiene [11], 2-methoxy- and 2-formyloxy-butadienes [12], and also in the condensation of 2-phenylbutadiene with acrylic acid, acrolein, propiolic acid, and styrene [11].

In the condensation of 2-methoxy- and 2-ethoxy-butadienes with acrolein, only the para-alkoxytetra-hydrobenzaldehydes were isolated [13]:
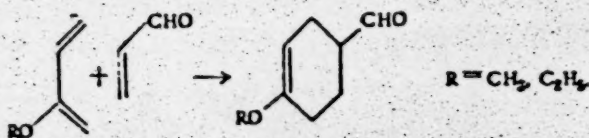
Our results, therefore, provide the first example of the formation of meta isomers in the condensation of 2-substituted butadienes in which the substituents are electronegative groups. Meta isomers are probably formed also in other cases, and only their low content in the reaction products has prevented their isolation.

EXPERIMENTAL

Preparation of 1,3,3-Trimethoxybutane. Nieuwland's catalyst [14], prepared from 4.5 ml of BF$_3 \cdot$ (C$_2$H$_5$)$_2$O, yellow mercuric oxide (15 g), trichloroacetic acid (2 g), and absolute methanol (10 ml), was introduced into a three-necked two-liter flask provided with mercury-sealed mechanical stirrer, tube for passing gas, reflux condenser, and thermometer; and absolute methanol (480 g, i.e. 15 moles) was then added. The solution obtained was stirred for nine hours, during which gaseous butenyne (280 g, i.e. 5.4 moles) was passed, the temperature was maintained at about 40° by the heat of reaction (it was sometimes necessary to apply cooling). On the next day the reaction mixture was stirred for a further four hours at 35-40°, and was then cooled and neutralized with sodium methoxide (16 ml of a 6% solution). The unchanged methanol was distilled off under reduced pressure. Fractionation of the residue yielded 483 g of 1,3,3-trimethoxybutane, b.p. 60-62°/19 mm, n_D^{23} 1.4112. The methanol that had been distilled off (90-120 g) was again distilled at normal pressure, a further 15 g of trimethoxybutane being isolated from the residue. The total yield of 1,3,3-trimethoxybutane was therefore 498 g, i.e. 67% on the amount of methanol taken, or about 80% when recovered methanol was taken into account. It was found that, if a further addition of 1 ml of BF$_3 \cdot$ (C$_2$H$_5$)$_2$O and 5 g of mercuric oxide is made toward the end of the reaction (when it dies down), the yield can be further increased by 5-7%, but difficulties then arise in the fractionation of the product (violent bumping).

Preparation of 2-Methoxy-1,3-butadiene (I). Diphenyl ether (10 g) and finely ground potassium hydrogen sulfate (0.5 g) were placed in a three-necked 250 ml flask fitted with thermometer, dropping funnel, and efficient fractionating column. The mixture was heated to 150°, and 1,3,3-trimethoxybutane was added at such a rate that the temperature of the vapor leaving was maintained at not higher than 62°. A mixture of 2-methoxy-1,3-butadiene, 2,4-dimethyl-1-butene, and methanol distilled over. As more and more trimethoxybutane was added, the mixture in the flask became darker in color owing to resin formation, the amount of methoxybutadiene in the distillate increased, and the temperature of the vapor leaving fell to 58-69°. After the addition of the first 150 g of trimethoxybutane, the process was stopped, and the distillate was transferred to a flask containing 5% sodium carbonate solution (20 ml). It was found that it was better to treat the distillate obtained from the first 150 g of trimethoxybutane separately and to subject it to further treatment with potassium hydrogen sulfate, it being found to contain appreciable amounts of dimethoxybutene.

In this reaction it is necessary to take care that the temperature of the vapor leaving does not rise above 59°. At a given bath temperature, it is easy to regulate the temperature of the vapor by means of the rate of addition of trimethoxybutane (25-30 g per hour). It is desirable to carry out the reaction in a number of such interruptions being quite permissible. The distillate was washed twice with twice its amount of a 1% solution of sodium carbonate, it was then dried with calcium chloride (20-25% on the weight of methoxybutadiene) and distilled through an efficient column. The fraction of b.p. 72-75° and n_D^{20} 1.4430-1.4450 was collected, this was found to be quite suitable for further synthesis; the yield was 65-70%. The high-boiling fractions were submitted to further reaction, thus yielding a further amount of methoxybutadiene and increasing the total yield to 80%.

Preparation of 2,3,4a,5,8,8a-Hexahydro-6-methoxy-8a-methyl-1(2H)-naphthalenone (III) and 2,3,4a,5,8,8a-hexahydro-7-methoxy-8a-methyl-1(2H)-naphthalenone (IIIa). 2-Methoxybutadiene (I) (15 g) and 2-methyl-2-cyclohexen-1-one (II) (120 g), prepared by the method described previously (b.p. 56°/9 mm, n_D^{20} 1.4865), were

heated in a metal ampoule in presence of 1% of diethylaniline in an atmosphere of carbon dioxide for 2 hours 30 minutes, the bath temperature being 260-270°. The excess of methylcyclohexenone was driven off under reduced pressure (107 g). The residues from four identical experiments were united and subjected to three successive fractionations. The following fractions were obtained:

Fraction I.   b.p. 73-90° at 13 mm; 10 g; n_D^{20} 1.4890

Fraction II. b.p. 60-90° at 1 mm; 16 g; n_D^{20} 1.5015

Fraction III. b.p. 90-100° at 1 mm; 43 g; n_D^{20} 1.5095

Fraction IV. b.p. 100-150° at 1 mm; 8 g; n_D^{20} 1.5135

Residue 55 g

Refractionation of Fraction (III) yielded 40 g of a mixture of the compounds (III) and (IIIA) having b.p. 92-95°/1 mm and n_D^{20} 1.6090. The yield was 64% on the methylcyclohexenone that reacted. Further fractionation of Fractions (II) and (IV) (united from many experiments) increased the yield of compounds (II) and (IIIA) to 54%. Numerous experiments were carried out under these conditions (about 160), and the yields were constantly reproduced: 27-40% on the 2-methoxybutadiene taken and 45-50% on the methylcyclohexenone that reacted. Reduction in duration of heating to 00 minutes and ten-fold dilution of the mixture had no appreciable effect on the yield. In this way about 1 kg of the hexahydromethoxymethyl-1(2H)-naphthalenones (III) and (IIIA) was obtained. The excess of 2-methyl-3-cyclohexen-1-one from 10-12 condensations was fractionated through a column in order to purify it and then used again in the condensation reaction.

The semicarbazone of the hexahydromethoxymethyl-1(2H)-naphthalenone (evidently of II) is formed very rapidly when the compound is mixed with an alcoholic solution of semicarbazide acetate. It forms fine glistening crystals, m.p. 208-209.5° (from a mixture of dioxane and methanol).

Found %:   C 62.1; 62.4; H 8.5; 8.2
$C_{13}H_{20}O_2N_3$ Calculated %: C 62.15   H 8.3

Hydrogenation of the Hexahydromethoxymethyl-1(2H)-naphthalenones (III and IIIA). The mixture of (III) and (IIIA) (6.1 g; b.p. 92-95°/1 mm; n_D^{20} 1.6090) dissolved in 10 ml of absolute dioxane was hydrogenated in presence of a Pd catalyst for 13 hours. The amount of hydrogen (20°, 700 mm) absorbed was 700 ml (570 ml was theoretically required). Vacuum fractionation of the product yielded 3.8 g of the corresponding octahydro-1(2H)-naphthalenone derivative (III) having b.p. 89-91° at 0.5 mm; n_D^{20} 1.4892; d_4^{20} 1.039; found MR_D 54.6; calculated MR_D 54.9. The semicarbazone formed fine white crystals (from 70% alcohol), m.p. 199-202° (decomp.).

Found %:   C 61.75; 61.8; H 9.3; 9.2
$C_{13}H_{23}O_2N_3$ Calculated %: C 61.65   H 9.15

In admixture with the semicarbazone of the original substance it melted at 186-192° (decomp.)

Preparation of 1-Ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6-methoxy-8a-methyl-1-naphthol (IV). Liquid ammonia (300 ml) was introduced into a three-necked liter flask, provided with mercury-sealed stirrer, dropping funnel, thermometer, and tube for passage of acetylene, and cooled with a mixture of solid carbon dioxide and ethanol (−70°). sodium (5 g) was added under stirring. Acetylene was passed at 20 liters per hour into the suspension formed, and after two hours a solution of 14 g of the hexahydromethoxymethyl-1(2H)-naphthalenones (III and IIIA) in 60 ml of absolute ether was added over a period of ten minutes. Passage of acetylene was continued further for four hours (2-3 liters per hour). The temperature being allowed to rise to −30°; finely ground ammonium chloride was then added, the mixture was set aside overnight. On the next day, water (100 ml) was added to the reaction mixture, which was then extracted three times with ether. The ether extracts were dried with magnesium sulfate and filtered. Ether was distilled off until crystals began to separate, and the mixture was then set aside over night. On the next day the crystals were filtered off under suction and washed three times with ether and petroleum ether. Three crystals (6 g) of m.p. 121-123° were isolated.

Crystallization from 5 ml of chloroform gave pure 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6-methoxy-8a-methyl-1-naphthol, m.p. 121-123°.

Found %:   C 76.0; H 9.05;
Calculated %: C   H 9.15

The mother liquor from the first crystallization was evaporated and vacuum-distilled, yielding 6 g of a mixture of the methoxy alcohols (IV) and (IVa) in the form of a colorless liquid of b.p. 119-121°/1 mm and n_D^{21} 1.5262. Replacement of sodium by potassium or lithium in this synthesis did not give improved results.

Hydrolysis of 1-Ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6-methoxy-8a-methyl-1-naphthol (IV) to Give 5-Ethynyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (V). A solution of 0.42 g of the ethynyloctahydromethoxymethylnaphthol (IV) in 5 ml of ether was shaken with 3 ml of 8% hydrochloric acid. Already after 20 minutes, white crystals began to precipitate. After two hours they were filtered off under suction, washed with ether and water, and dried in a desiccator. The product was 0.39 g of 5-ethynyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (V), m.p. 155-156°, which has been described previously [1]. The yield was thus almost quantitative.

Preparation of 5-Ethynyloctahydro-6-hydroxy-4a-methyl-2(1H)-naphthalenone (V) and 8-Ethynyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone (Va). Liquid ammonia (850 ml) was introduced into a 2-liter flask provided with mercury-sealed stirrer, dropping funnel, thermometer, and tube for passage of acetylene, and cooled with a mixture of solid carbon dioxide and methanol (−70°); sodium (17 g) was added under stirring. Acetylene (about 40 liters) was passed in the course of one hour, and the rate of passage was then reduced to 3-5 liters per hour. To the suspension of sodium acetylide formed, a solution of 80 g of the mixture of hexahydromethoxymethyl-1(2H)-naphthalenones (II and IIa) in 250 ml of absolute ether was added over a period of one hour. Passage of acetylene (3-5 liters per hour) was continued for six hours, and the mixture was then set aside at −70° overnight. On the next day the mixture was stirred for five hours, acetylene being passed at 2-3 liters per hour and the temperature being allowed to rise to −35°. Finely ground ammonium chloride (60 g) was then added, a little at a time, and the mixture was then set aside overnight, the ammonia being allowed to evaporate away.

On the next day, ether (200 ml) was added, and the mixture was treated with ice water (80 ml). The ether layer was separated, and the aqueous layer was extracted three times with ether (150 ml altogether). The united ether extracts were evaporated down to a volume of 180-200 ml. 1% hydrochloric acid (100 ml) was added, and the mixture was stirred vigorously for three hours. Already after thirty minutes light-yellow crystals began to be precipitated. The precipitated crystals were filtered off under suction, washed four times with cold ether and twice with cold water, and dried to constant weight in a desiccator. The weight of hydroxy ketone (V) obtained in this way was 34-39 g (varying in different experiments); it melted at 154-155.5°, and was sufficiently pure for the subsequent hydrogenation treatment. A single crystallization from alcohol or benzene gave a product of constant melting point (158°).

Ether was removed from the mother liquor by distillation, petroleum ether was added, and the mixture was set aside overnight. By the next day crystals (6-8 g) had formed which consisted essentially of 8-ethynyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone (Va), m.p. 139-142°. Crystallization from alcohol yielded the pure isomer (Va), m.p. 144°.

Found %: C 75.9; 75.9; H 8.8; 8.9
$C_{13}H_{18}O_2$. Calculated %: C 75.7; H 8.8

The mother liquor after removal of solvents weighed 32-38 g, and on distillation it yielded 13-16 g of a liquid mixture of the hydroxy ketones (V) and (Va) having b.p. 134-136°/1.5 mm and n_D^{20} 1.5280. Analysis of this mixture of liquid hydroxy ketones gave the following results:

Found %: C 75.55; 75.5; H 9.15; 8.95
$C_{13}H_{18}O_2$. Calculated %: C 75.7; H 8.8

This mixture, like the pure hydroxy ketones (V) and (Va), gave a voluminous white precipitate with an ammoniacal solution of silver oxide (test for acetylenic hydrogen).

Exhaustive Hydrogenation of the Hydroxy Ketones (V) and (Va). The hydroxy ketone (V) (420 mg) dissolved in alcohol (5 ml) was hydrogenated in presence of platinum by Adam's method. Hydrogenation began immediately and was complete in 7 minutes, 100 ml (22°, 700 mm) of hydrogen being absorbed, as required by theory. The solution was filtered and allowed to evaporate. The readily soluble 5-ethyloctahydro-5-hydroxy-4a-methyl-2(1H)-naphthalenone (X) was isolated as white crystals (50 mg), m.p. 127-128°.

Found %: C 74.2; 74.0; H 10.7; 10.8
$C_{13}H_{20}O_2$ Calculated %: C 74.25; H 10.6

The hydroxy ketone (Va) was hydrogenated in a similar way, yielding 8-ethyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone (Xa) (0.6 g from 1.0 g of hydroxy ketone) in the form of white crystals, m.p. 86°.

Found %: C 74.2; 74.1; H 10.5; 10.4
$C_{13}H_{22}O_2$ Calculated %: C 74.25; H 10.5

In the hydrogenation of 2.1 g of the liquid mixture of hydroxy ketones, 465 ml (18°, 760 mm) of hydrogen was absorbed, 460 ml being theoretically required.

Selective Hydrogenation of 5-Ethynyloctahydro-5-hydroxy-8a-methyl-2(1H)-naphthalenone (V) to Give Octa-hydro-5-hydroxy-8a-methyl-5-vinyl-2(1H)-naphthalenone (VI). The substance (V) (12.7 g) dissolved in 100 ml of dioxane was hydrogenated in presence of palladium carried on calcium carbonate until one molecule of hydrogen (1470 ml; 18°, 760 mm) had been absorbed. The solution was filtered, and the dioxane was driven off under reduced pressure. The light-yellow viscous mass that remained very slowly (after a week) crystallized out, but for the preparation of the dienone (VII) the product was used without being crystallized. The pure octahydro-5-hydroxy-8a-methyl-5-vinyl-2(1H)-naphthalenone (VI) melted at 111-112° (two crystallizations from petroleum ether). This alcohol has been previously prepared in our laboratory [1] but was then characterized as a liquid.

Selective Hydrogenation of 8-Ethynyloctahydro-8-hydroxy-8a-methyl-2(1H)-naphthalenone (Va) to Give Octahydro-8-hydroxy-8a-methyl-8-vinyl-2(1H)-naphthalenone (VIa). The hydrogenation of the substance (Va) was carried out in a similar way. Crystallization was found to occur immediately after removal of solvent; 27.7 g of the alcohol (Va) yielded 19.6 g of crystals, m.p. 113-115°. The pure alcohol (VIa) melted at 114-115°.

Found %: C 75.15; H 10.1
$C_{13}H_{20}O_2$ Calculated %: C 75.0; H 9.7

Dehydration of Octahydro-5-hydroxy-8a-methyl-5-vinyl-2(1H)-naphthalenone (VI). A mixture of 16 g of the substance (VI), 8 g of finely ground potassium hydrogen sulfate, and 0.05 g of pyrogallol was heated at 140-145° for 30 minutes under reduced pressure (40-45 mm). The weight of water separated was 1.3 g (theoretical amount 1.4 g). The reaction mixture was cooled and extracted with ether; the ether was driven off, and the product was vacuum-distilled, yielding 10 g (67%) of 3,4,4a,7,8,8a-hexahydro-8a-methyl-5-vinyl-2(1H)naphthalenone (VII) in the form of a thick colorless liquid having a fairly pleasant odor. It boiled at 114-117°/3mm, or 100-103°/1mm, and had n_D^{18} 1.5260; d_4^{18} 1.022. The semicarbazone (from 80% alcohol) melted at 174.5-176°.

Found %: C 68.0; 68.15; H 8.8; 8.8
$C_{14}H_{21}ON_3$ Calculated %: C 68.0; H 8.6

Dehydration of Octahydro-8-hydroxy-8a-methyl-8-vinyl-2(1H)-naphthalenone (VIa). This dehydration was performed in the manner described above from 8.6 g of the substance VIa, the product being 3,4,4a,5,6,8a-hexahydro-8a-methyl-8-vinyl-2(1H)-naphthalenone (VIIa) (5.9 g, 74%), which is a thick colorless liquid having a fairly pleasant odor, b.p. 94-96°/0.5 mm, n_D^{18} 1.5270. The semicarbazone (from a mixture of methanol and dioxane) melted at 196-197°.

Found %: C 68.1; H 8.7
$C_{14}H_{21}ON_3$ Calculated %: C 68.0; H 8.6

Selective Hydrogenation of the Liquid Mixture of Acetylenic Hydroxy Ketones (V) and (Va). The substance (7.6 g) dissolved in alcohol (20 ml) was hydrogenated in presence of palladium carried on calcium carbonate until one molecule of hydrogen (840 ml, 18°, 760 mm) had been absorbed. The solution was filtered, and alcohol was distilled off under reduced pressure; the residue was diluted with ether (5 ml) and set aside at 0° to crystallize. After two months the mixture had partially crystallized out, and the crystals were pressed off under suction and washed with cold ether. The product was octahydro-8-hydroxy-8a-methyl-8-vinyl-2(1H)-naphthalenone (VIa) (1.7 g), m.p. 114-115°. In admixture with the sample obtained previously it showed no depression in melting point.

Dehydration of the Liquid Mixture of Vinyl Hydroxy Ketones. The mother liquor from the preceding experiment was dehydrated with the aid of potassium hydrogen sulfate, as described above, yielding 2.4 g (46%) of a mixture of the dienones (VII) and (VIIa), b.p. 114-119°/2 mm, n_D^{18} 1.5260.

Condensation of the Dienone (VII) with Maleic Anhydride. The dienone (VII) (8.8 g) was mixed with p...

anhydride (0.4 g). Reaction set in very quickly, the temperature rising to 50°. The mixture was set aside for 12 hours but crystallization did not occur, in spite of addition of solvent and cooling. Alcohol (3 ml) and 20% caustic potash (3 ml) were added to the mixture, which was then set aside for two hours. The homogeneous solution was diluted with an equal volume of water and extracted with ether, and the aqueous solution was acidified to Congo red with concentrated hydrochloric acid. A light-yellow sticky mass of polymer came down. The aqueous solution was decanted and set aside in the cold. Crystals (0.12 g) soon made their appearance, and they were recrystallized from 6 ml of 50% acetic acid, yielding 0.10 g of fine white crystals of the previously described [?] dicarboxylic acid (XI) which decomposes at 200-202.5° (rapid heating). Condensation in xylene at 140° gave similar results.

Condensation of the Dienone (VIIa) with Maleic Anhydride. In a similar way, the dienone (VIIa) (0.6 g) yielded the dicarboxylic acid (XIa) (0.08g). On being heated rapidly, the acid melted with decomposition at 203°, but the material became transparent only at 210°.

<div align="center">

Found %: C 66.3; H 7.3

$C_{13}H_{20}O_2$, Calculated %: C 66.65; H 7.2
</div>

The Splitting of Acetylene from 5-Ethynyloctahydro-6-hydroxy-4a-methyl-2(1H)-naphthalenone (V). The hydroxy ketone (V) (2g), toluene (10 ml), and powdered potassium hydroxide (0.05 g) were heated at 110° for 30 minutes. There was vigorous evolution of acetylene (detected by the Ilosvay reagent). The solution was cooled and washed with water; the solvent was driven off, and an attempt was made to distill the residue under reduced pressure. Only an insignificant amount of hexahydro-8a-methyl-1,6 (2H, 5H)-naphthalenedione (VIII) crystals, m.p. 60-62°, came over at 180/2 mm. In admixture with a known sample there was no depression of melting point. The residue was an undistillable resin. Similar results were obtained when the hydroxy ketone was heated with sodium amyloxide.

Preparation of 1,2,3,4,4a,7,8,8a-Octahydro-2,4a-dimethyl-5-vinyl-2-naphthol (XII). A solution of the dienone (VI) (5.0 g) in ether (20 ml) was added at 5-10° over a period of ten minutes to a Grignard reagent prepared in the usual way from magnesium (3 g), methyl bromide (13 g), and absolute ether (100 ml). The solution was boiled for five minutes, cooled, and decomposed, firstly with ice, and then with 20% hydrochloric acid, until the flocs of magnesium hydroxide had disappeared. Careful extraction and distillation yielded 4.9 g (90%) of the dienol (XII) in the form of a thick, colorless liquid, b.p. 91-94°/0.5 mm, n_D^{18} 1.5260.

<div align="center">

Found %: C 81.5; 81.3; H 11.05; 10.9

$C_{14}H_{22}O$, Calculated %: C 81.5; H 10.75
</div>

Preparation of 1,2,3,5,4a,8,6,8a-Octahydro-2,8a-dimethyl-6-vinyl-2-naphthol (XIIa). By a similar method, from 4 g of the dienone (VIIa), 3.8 g (87%) of the dienol (XIIa), b.p. 92-96°/0.5 mm and n_D^{18} 1.5235, was obtained.

<div align="center">

Found %: C 81.5; H 11.0

$C_{14}H_{22}O$, Calculated %: C 81.5; H 10.75
</div>

Dehydration of 1,2,3,4,4a,7,8,8a-Octahydro-2,4a-dimethyl-5-vinyl-2-naphthol (XII). The dienol (XII) (4.9 g), potassium hydrogen sulfate (2.5 g), and pyrogallol (0.05 g) were heated for 15 minutes under reduced pressure (45 mm) at 140° (at 150° toward the end). The usual treatment and fractionation yielded 2.9 g (66%) of 3,4,4a,7,8,8a-hexahydro-6,8a-dimethyl-1-vinylnaphthalene (XVI) in the form of a colorless mobile liquid of pleasant odor, b.p. 70-72°/1 mm; n_D^{18} 1.5210; d 0.940; found MR_D 61.1; calculated MR_D 61.05.

<div align="center">

Found %: C 89.0; 89.3; H 10.6; 10.4

$C_{14}H_{20}$, Calculated %: C 89.3; H 10.7
</div>

Dehydration of 1,2,3,4,4a,5,6,8a-Octahydro-2,8a-dimethyl-8-vinyl-2-naphthol (XIIa). The procedure was similar to that of the previous experiment. From 3.7 g of the dienol (XIIa), 2.0 g of 1,2,4a,5,6,8a-hexahydro-4a-7-dimethyl-1-vinylnaphthalene (XVIa), b.p. 68-70°/0.5 mm and n_D^{18} 1.5220 was obtained.

<div align="center">

Found %: C 88.6; H 10.7

$C_{14}H_{20}$, Calculated %: C 89.3; H 10.7
</div>

Condensation of the Dienol (XII) with Dimethyl Maleate. A mixture of the dienol (XII) (5.8 g) and dimethyl maleate (5 g; b.p. 84°/10 mm; n_D^{18} 1.4416) was heated at 100° for six hours. The excess of the ester was

driven off under reduced pressure (1 mm) on a water bath (12.5 g). The residue was heated with finely ground potassium hydrogen sulfate (2.5 g) and pyrogallol (0.05 g) at 160-170° for 15 minutes under reduced pressure (25 mm). After the usual treatment, the product was vacuum-distilled.

Fraction I.   b.p. 77-84°/1 mm; 1.2 g; n_D^{18} 1.5235.
Fraction II: b.p. 84-165°/1 mm; 0.2 g
Fraction III: b.p. 165-170°/1 mm; 4.3 g; n_D^{18} 1.5200
Residue: 1.5 g

Fraction III was the dicarboxylic ester XIV. It was a thick, odorless glycerol-like liquid.

Found %: C 72.9; H 8.5
$C_{16}H_{26}O_4$. Calculated %: C 72.3; H 8.5

Fraction III was dissolved in alcohol (10 ml), and 40% caustic soda (4 ml) was added. The solution was heated at 80-85° for three hours and then cooled. Water (10 ml) was added, the mixture was extracted with ether, and the aqueous layer was poured, under cooling, into 20% hydrochloric acid (10 ml). An oil separated, and this quickly solidified, giving a fine powder. Addition of 5 ml of ether accelerated this process. The crystals were filtered off under suction and washed several times with ether and with water. The product was the acid (XV) in the form of a white powder, which did not melt below 200°. A low carbon content was obtained in the analysis.

Condensation of the Dienol (XIIa) with Dimethyl Maleate. The procedure was similar to that in the previous experiment. From 3.7 g of the dienol (XIIa), 2.6 g of the ester (XIVa) was obtained. Hydrolysis yielded a viscous mass, which could not be caused to crystallize.

Dehydrogenation of the Acid (XV). A mixture of the acid (XV) (2.1 g), dry benzene (12 g), and 10% palladinized charcoal (1 g) was heated in an atmosphere of nitrogen in a rotating autoclave at 370° for 11 hours. Even then, the reaction was not complete, for after filtration, washing of the benzene solution with alkali, and removal of the solvent, only 0.4 g of a light-brown liquid remained. After one day, it had partially crystallized out. The crystals were filtered off and washed with a small amount of a mixture of petroleum ether and benzene (10:1). 2-Methylphenanthrene (XVI) (50 mg) was obtained in the form of fine, white crystals, m.p. 57-58.5°.

Found %: C 93.4; H 6.35
$C_{15}H_{12}$ Calculated %: C 93.7; H 6.3

The picrate formed (from methanol) light-brown needles, m.p. 115-117°. Dehydrogenation of the acid (XVa), which was isolated in an impure form (viscous mass), did not give clear results: it was not found possible to isolate a crystalline hydrocarbon.

Condensation of 3,4,4a,7,8,8a-Hexahydro-6,8a-dimethyl-1-vinylnaphthalene (XVII) with 2-Cyclohexen-1-one. The triene (XVII) (1.2 g) and freshly distilled 2-cyclohexen-1-one (3.1 g, b.p. 63°/22 mm; n_D^{18} 1.4870) were heated in a sealed tube in an atmosphere of carbon dioxide at 200° for four hours. Fractionation gave the following fractions:

Fraction I: b.p. 50-60°/10 mm; 1.6 g
Fraction II: b.p. 40-150°/1 mm; 1.0 g
Fraction III: b.p. 150-155°/1 mm; 0.5 g
Residue: 0.7 g

Fraction III consisted mainly of the ketone (XVIII) contaminated with self-condensation products of cyclohexenone (this is shown by the low carbon content). It was used in further reactions without purification.

Condensation of 1,2,4a,5,6,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XVIIa) with 2-Cyclohexen-1-one. The procedure was similar to that in the preceding experiment. From 2.2 g of the triene, 1.2 g of crude ketone (XVIIIa) b.p. 145-155°/1 mm, was obtained. It was used in further reactions without purification.

Kizhner Reduction of the Ketone (XVIII) and Dehydrogenation of the Hydrocarbon Formed (XIX). Crude ketone (XVIII) (0.5 g) was mixed with diethylene glycol (3 ml), hydrazine hydrate (0.4 ml) was added, and the mixture was heated for five minutes. The mixture was transferred to a Favorsky flask provided with ground joints, a solution of sodium (0.4 g) in diethylene glycol (10 ml) was added, and the turbid solution was heated in a feeble stream of nitrogen for 10 hours at 200-205° and for 3 hours at 220°. In the course of this treatment a small amount of distillate came off. The reaction mixture was diluted with twice its volume of water, and the solution obtained was extracted with ether. The ether extract was washed twice with 10% hydrochloric acid and with water. The

ether solution was dried with magnesium sulfate, the ether was driven off, and the residue was evaporated under reduced pressure on a water bath, yielding 0.4 g of a thick light-brown liquid, which was impure hydrocarbon XIX. Without being purified, it was hydrogenated as follows.

The hydrocarbon (XIX) was dissolved in 14 ml of benzene, 0.3 g of 10% palladinized charcoal was added, and the mixture was heated in an atmosphere of nitrogen in a rotating autoclave at 350° for six hours. The mixture was filtered, benzene was removed under reduced pressure, and a residue was obtained that partially crystallized out. The crystals were filtered off under suction and were washed four times with petroleum ether. The product was 14 mg of 2-methylchrysene in the form of white plates, m.p. 222-223°. The picrate formed light-orange needles, m.p. 145.5-146°.

<div align="center">

Found %: C 94.45; 94.1; H 6.0; 6.1

$C_{19}H_{14}$ Calculated %: C 94.2; H 5.8

</div>

Kizhner Reduction of the Ketone (XVIIIa) and Dehydrogenation of the Hydrocarbon Formed (XIXa). The procedure was similar to that in the preceding experiment, but crude hydrocarbon (XIXa) distilled over. From 1.2 g of crude ketone (VIIIa), 0.45 g of hydrocarbon (XIXa), b.p. 125-130°/0.5 mm, was obtained; it was dissolved in 10 ml of benzene, 0.3 g of palladium on charcoal (10% Pd) was added, and the mixture was heated in an atmosphere of nitrogen in a rotating autoclave for 3 hours at 320° and 3.5 hours at 350°. The solution was filtered, the benzene was driven off, and the residue was dissolved in 2 ml of petroleum ether and cooled to −15°. Crystals were precipitated, and after two hours these were filtered off under suction and washed with cold petroleum ether. The product was 15 mg of 3-methylchrysene, m.p. 166-169°. The picrate formed orange needles, m.p. 160-161°.

SUMMARY

1. A detailed investigation has been made of the conditions for the condensation of 2-methyl-2-cyclo-hexen-1-one (II) with 2-methoxy-1,3-butadiene (I).

2. It has been shown that this condensation proceeds in two directions with formation of 2,3,4a,5,8,8a-hexahydro-6-methoxy-8a-methyl-1(2H)-naphthalenone (III) and 2,3,4a,5,8,8a-hexahydro-7-methoxy-8a-methyl-1(2H)-naphthalenone (IIIa) in a ratio of approximately 5:1. The yield of condensation products has been increased from 25 to 45.6%.

3. A detailed study has been made of the condensation of the compounds III and IIIa with alkali-metal acetylides in liquid ammonia. By this means yields of 50-55% of the acetylenic hydroxy ketones (V) and (Va) have been obtained, and these have been hydrogenated selectively in the presence of a Pd catalyst, yielding the vinyl hydroxy ketones (VI) and (VIa), which have been dehydrated with potassium hydrogen sulfate to give the dienones (VII) and (VIIa). The structures of these dienones and related compounds have been rigorously proved by converting them into known methylchrysenes (XX and XXa), and also by converting the dienone (VII) into the known 2-methylphenanthrene.

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CATALYTIC AMINATION OF KETONES OF VARIOUS STRUCTURES

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In a previous investigation [1] we have shown that reductive amination of acetone and cyclohexanone in presence of platinized silica gel gives the corresponding primary amines in good yield. This fact prompted us to continue the investigation for other ketones in order to determine the effect of the number of carbon atoms in ketone molecules, having like or unlike radicals, on the yield of amine in the reductive amination reaction. In the present investigation we have investigated the reductive amination of 3-pentanone, 4-heptanone, 2-butanone, 2-octanone, and cyclopentanone in presence of platinized silica gel.

EXPERIMENTAL

Ketone vapor, together with excess of ammonia and hydrogen, was passed through a quartz tube containing 80 ml of platinized silica gel, which was mounted in an electric furnace fitted with a thermoregulator. The reaction products passed to a receiver cooled with snow and salt. The duration of each experiment was 30 minutes. The properties of the ketones investigated are given in Table 1.

TABLE 1

Properties of Investigated Ketones

Ketone	Our preparation				Data in literature			References
	B.p. (°C)	Pressure (mm Hg)	d_4^{15}	n_D^{15}	B.p. (°C, corr.)	Specific gravity	Refractive index	
3-Pentanone	101	758	0.8149	1.3921	101.08	$d_4^{19.1}$ 0.8159	$n_D^{19.1}$ 1.39265	[2 and 3]
4-Heptanone	143	759	0.8203	1.4064	143.52	d_4^{20} 0.8160	n_D 1.4047	[2 and 3]
2-Butanone	77-78	756	0.8087	1.3774	78.6	d^{18} 0.8054	n_D^{19} 1.3807	[4 and 5]
2-Octanone	171	752	0.8193	1.4158	172.92	d_4^{20} 0.8185	n_D^{18} 1.41013	[2 and 6]
Cyclopentanone	128-129	748	0.9484	1.4363	129	d_4^{20} 0.9480	n_D^{19} 1.4366	[7]

The condensates obtained were dried with solid caustic potash, and the total contents of amine nitrogen were determined by Francois' method [8]

Information on experimental conditions and the results of the reductive amination of the above ketones are given in Table 2 on page 82.

Experiment No. 18, on the amination of 2-butanone at 200°, was carried out for 4 hours 30 min, in order to find out how long the catalyst continued to function. Separate portions of condensate were collected every 30 minutes, and analyses for amine-nitrogen content were carried out for the 1st, 3rd, 5th, 7th, and 9th portions. Experiments having the same purpose were carried out also with 2-octanone at 200°. One of these (No. 19) was performed with fresh catalyst, and another (No. 24) with previously used, nonregenerated catalyst.

The experiments showed that in the amination of cyclopentanone the catalyst was very quickly covered with resin, so that the pieces became stuck together. In this case, therefore, the catalyst was either extracted after each experiment to remove the greater part of the resin, and was then regenerated by roasting and blowing with air.

The condensates from the amination experiments on 2-butanone, 3-pentanone, and 4-heptanone, which contained considerable amounts of amine nitrogen, were investigated for the isolation of their components and their characterization. For this purpose, the condensate was acidified with dilute hydrochloric acid, which caused the liquid to separate into two layers. The upper layer contained unchanged ketone, and the lower layer contained amines in the form of their water-soluble hydrochlorides, in admixture with a little ketone; which was distilled off and added to the ketone layer. The unchanged ketone was dried and distilled. The aqueous solution of amine hydrochlorides was evaporated down to low volume, and excess of solid caustic alkali was added. The amine that separated was dried with caustic potash and distilled.

TABLE 3
Reductive Amination of Ketones

Expt. No.	Temp. (°C)	Amt. taken for reaction			Amt. of condensate(g)		Amine-nitrogen content(%)	Amine content of condensate (%)
		Ketone (g)	Ammonia (g)	Hydrogen (liters)	Crude	After drying		
3-Pentanone								
1	140	6.5	3.7	3.8	6.0	5.9	4.53	28.1
2	170	6.5	3.7	3.8	6.5	6.2	5.31	32.9
3	200	6.5	3.7	3.8	7.9	7.7	4.34	26.9
4	230	6.5	3.7	3.8	7.2	6.5	4.10	25.4
5	260	6.5	3.7	3.8	7.3	6.1	5.49	34.0
6	290	6.5	3.7	3.8	7.8	6.1	3.22	20.0
4-Heptanone								
7	170	6.6	3.0	3.7	5.9	4.9	3.76	30.8
8	200	6.6	3.0	3.7	6.8	5.7	5.05	41.4
9	230	6.6	3.0	3.7	6.9	6.8	4.11	33.7
10	260	6.6	3.0	3.7	7.4	6.5	2.96	24.3
2-Butanone								
11	150	6.4	4.5	3.5	6.2	4.2	2.47	12.8
12	170	6.4	4.2	3.5	6.6	6.0	3.38	17.6
13	200	6.4	4.3	3.5	6.5	6.0	4.19	21.7
14	230	6.4	4.5	3.5	6.7	6.2	3.85	20.0
15	260	6.4	4.5	3.5	6.5	6.0	2.98	15.5
16	290	6.4	4.5	3.5	6.6	5.8	2 87	14.9
17	320	6.4	4.5	3.5	6.7	5.9	2.79	14.5
18-1	200	6.4	4.5	3.5	6.2	5.8	4.40	22.9
18-3	200	6.5	4.5	3.5	6.5	6.0	4.29	22.3
18-5	200	6.5	4.5	3.5	6.5	6.0	3.79	19.7
18-7	200	6.5	4.5	3.5	6.5	6.1	3.29	17.1
18-9	200	6.5	4.5	3.5	6.4	6.0	3.28	17.1
2-Octanone								
19	200	6.6	2.0	2.5	6.6	6.0	1.83	16.8
20	230	6.6	2.0	2.5	6.6	6.1	1.73	16.1
21	260	6.6	2.0	2.5	8.1	7.0	1.56	14.3
22	290	6.6	2.0	2.5	8.1	7.0	1.17	10.8
23	320	6.6	2.0	2.5	7.3	6.2	1.16	10.7
24	200	6.6	2.0	2.5	6.0	5.5	0.96	8.8
Cyclopentanone								
25	150	7.6	4.2	3.2	3.0	1.0	1.63	9.9
26	170	7.6	4.2	3.2	3.8	1.2	1.85	11.3
27	200	7.6	4.2	3.2	4.5	2.3	1.29	7.9
28	230	8.1	4.5	3.2	3.4	1.7	1.62	9.9
29	260	7.9	4.2	3.2	5.0	3.4	1.41	8.6
30	290	7.9	4.5	3.2	6.1	4.0	0.70	4.3
31	320	7.6	4.2	3.2	8.2	6.1	0.42	2.6

From 22.0 g of united condensate obtained from the reductive amination of 3-pentanone and containing 4.51% of amine nitrogen, 13.0 g of unchanged ketone and 4.7 g of amine were isolated. The isolated ketone had b.p. 100°/758 mm, d_4^{18} 0.8148, and n_D^{18} 1.3922; it had remained, therefore, fairly pure. The amine had b.p. 86°/746 mm, d_4^{18} 0.7479 and n_D^{18} 1.4063. Analysis gave:

<div align="center">

Found %: C 68.90; H 15.09; N 16.27

$C_5H_{13}N$ Calculated %: C 68.89; H 15.04; N 16.07

</div>

The amine obtained, therefore, was close in properties and composition to 1-ethylpropylamine, for which the literature gives b.p. 90-91° and d_4^{20} 0.7478 [9].

From 15.2 g of condensate from the reductive amination of 4-heptanone (amine-nitrogen content 4.15%), 8.0 g of unchanged ketone and 4.5 g of amine were isolated. The isolated ketone had b.p. 143°/753 mm, d_4^{19} 0.8205 and n_D^{19} 1.4062; these properties correspond to the original 4-heptanone. The amine obtained boiled over the range 138-140°/760 mm and had d_4^{19} 0.7657 and n_D^{18} 1.4178.

<div align="center">

Found %: C 72.98; H 14.59; N 12.15

$C_7H_{17}N$ Calculated %: C 72.95; H 14.89; N 12.16

</div>

In its properties and analysis the amine obtained corresponded to 1-propylbutylamine, for which the literature [10] gives: b.p. 140-141°/745 mm and d_4^{15} 0.7671.

From 52.1 g of unied condensate containing 3.56% of amine nitrogen, which was obtained by reductive amination of 2-butanone, 31.5 g of unchanged ketone and 8 g of amine were isolated. The ketone had b.p. 77-78°/746, d_4^{19} 0.8084 and n_D^{19} 1.3766, which correspond to the original 2-butanone. The amine obtained had b. p. 61-63°/750 mm, d_4^{19} 0.7155 and n_D^{15} 1.3948.

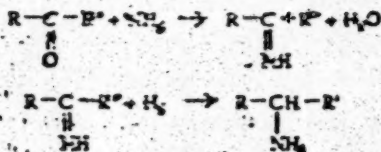<div align="center">

Found %: C 65.56; H 15.19; N 19.08

$C_4H_{11}N$ Calculated %: C 65.67; H 15.17; N 19.16

</div>

In its properties and analysis the synthesized amine was very close to 1-methylpropylamine, which, according to the literature, has b.p. 63°/760 mm [11], d_4^{15} 0.718 [9] and n_D^{15} 1.3960 [12].

The yields of these three amines, based on the amounts of ketone that reacted, were: 1-ethylpropylamine, 51.6%; 1-propylbutylamine, 64.2% and 1-methylpropylamine, 46.3%. It may be noted, for comparison, that in the reductive amination of acetone [1] at 240°, the condensate contained 9% of amine nitrogen, which corresponds to a 38% content of isopropylamine, and in the experiments with cyclohexanone [1] the condensate contained 12.7% of amine nitrogen, or 89.0% of cyclohexylamine.

DISCUSSION OF RESULTS

The experiments show that, over a wide range of temperatures (140-320°), reductive amination of ketones over platinized silica gel leads to the formation of the corresponding primary amines. The reactions occurring may be expressed as follows:

$$R-C-R' + NH_3 \rightarrow R-C-R' + H_2O$$
$$\underset{O}{\|} \qquad \underset{NH}{\|}$$

$$R-C-R' + H_2 \rightarrow R-CH-R'$$
$$\underset{NH}{\|} \qquad \underset{NH_2}{|}$$

The optimum temperature for the reaction lies in the range 170-240°; it is about 240° for acetone, about 200° for 2-butanone and 4-heptanone, and about 170° for 3-pentanone. Rise in temperature above 240° leads to a reduction in the amount of condensate and to the formation of resinous products, which cause a rapid fall in the activity of the catalyst. As regards the working life of the catalyst, the experiments on the reductive amination of acetone and 2-butanone show that platinized silica gel does not lose its activity for at least 4 hr, 30 min, and that it can be readily regenerated by heating in a stream of air.

The structure of the ketone and the length of its carbon chain have a considerable effect on the yield of amine. The ketones investigated may be divided into three groups: aliphatic ketones having like radicals, aliphatic ketones having unlike radicals, and ketones of the alicyclic series. Ketones of the first group (acetone, 3-pentanone, 4-heptanone) are readily aminated and give the highest yields of the corresponding amines. In the experiments with these ketones, condensates having amine contents of 34-41.4% were obtained.

Ketones of the second group (2-butanone, 2-octanone) give lower yields of amines than ketones of the first group, condensates having amine contents of 16.1-21.7% being obtained. The experiments with 2-octanone indicate

that an appreciable increase in the number of carbon atoms in one of the radicals of the ketone, in comparison with the other, results in an appreciable reduction in the yield of amine.

As regards alicyclic ketones, the experiments show that in this series the yield of amine depends on the stability of the ketone under the given conditions. Cyclohexanone, which does not resinify under the conditions of reductive amination, gives a high yield of cyclohexylamine. Cyclopentanone, which readily undergoes auto-condensation under the amination conditions, gives catalyzates having a low (not above 11.3%) content of cyclopentylamine.

SUMMARY

1. Reductive amination of ketones in presence of platinized silica gel gives only primary amines.

2. The optimum reaction temperature lies in the range 170-240°.

3. Aliphatic ketones having like radicals give higher yields of amines than ketones having unlike radicals.

4. Equal increases in the numbers of carbon atoms of the two identical radicals of a ketone do not lead to reduction in yield of amine.

5. Increase in the number of carbon atoms in only one of the radicals of the ketone leads to a reduction in the yield of amine. This reduction in yield is the greater, the greater the difference in the numbers of carbon atoms in the two radicals of the ketone.

6. In the reductive amination reaction, cyclopentanone gives insignificant yields of amine, owing to the occurrence under these conditions of condensation and resinification reactions.

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HYDROGENATING AND DEHYDROGENATING POWER
OF NICKEL CATALYSTS ON VARIOUS CARRIERS

N. I. Shuikin, Kh. M. Minachev, and L. M. Feofanova

Thanks to the work of Zelinsky and coworkers, nickel catalysts on various carriers (aluminum oxide, silica gel, activated charcoal) have received wide application in the practice of hydrogenation and dehydrogenation catalysis. It should be noted, however, that nickel catalysts on carriers have generally been prepared with a relatively high nickel content — up to 50% [1]. At such a high nickel content, hydrocarbons undergo considerable breakdown under dehydrogenation conditions at 300° and above. Thus, one of us [2] has shown that when methylcyclohexane is passed at 330° over a Ni/Al₂O₃ catalyst containing 50% of nickel, the gas leaving consists of 57.1% of hydrogen and 42.1% of methane; at 400°, cyclohexane is broken down completely to methane and hydrogen.

Gaverdovskaya [3] has observed that, already at 300°, a nickel catalyst (47% of nickel on silica gel), causes the breakdown of about 20% of cyclohexane. Also, it should be noted that nickel catalysts of high nickel content (of the order of 50%) lose their activity much more rapidly than catalysts of lower active nickel content.

It was shown in one of our investigations [4] that nickel catalysts prepared by impregnation of active charcoal with nickel nitrate solution and containing from 4 to 0.5% nickel are very efficient for the hydrogenation of the benzene ring. Their activity for dehydrogenation reactions, however, is much below the optimum, and this method of preparation permits us to obtain highly active catalysts only for hydrogenation purposes. In this investigation we decided to study the hydrogenating and dehydrogenating powers of nickel catalysts containing from 12 to 20% of nickel on various carriers.

Apart from the paper of Gaverdovskaya [3] already mentioned, there are practically no data in the literature on the activity and stability of nickel catalysts prepared on various carriers. Gaverdovskaya attempted to determine the influence of the carrier on the activity of a nickel catalyst. With this objective, a series of catalysts was prepared: they consisted of nickel precipitated on Al₂O₃, SiO₂, asbestos, active charcoal, Cr₂O₃, and ZnO. The most active for the dehydrogenation of the cyclohexane ring were the first two catalysts, and the least active were nickel on ZnO and nickel on active charcoal. The author was not successful in establishing the relation of the dehydrogenating power of a nickel catalyst to the chemical nature of the carrier, for different methods were used for the preparation of the various catalysts. Also, the catalysts prepared and investigated by Gaverdovskaya varied greatly in nickel content (from 4.3 to 47.1%).

Our investigation of the properties of nickel catalysts precipitated on Al₂O₃, ZnO, Cr₂O₃, MgO, and Fe₂O₃ has shown that the highest dehydrogenating activity is exhibited by nickel on Al₂O₃ and on ZnO, and the lowest activity by nickel precipitated on ferric oxide. Catalysts containing 11-19% of nickel precipitated on Al₂O₃ or ZnO dehydrogenate cyclohexane to the extent of 80-90% at 300°; under the same conditions, nickel on ferric oxide dehydrogenates cyclohexane only to the extent of 10%. The degree of conversion of cyclohexane over the same catalyst at 400° was 80%. All the catalysts studied, with the exception of Ni on Fe₂O₃, have high hydrogenating power and preserve it for a long time.

In the reduction of the catalysts a very interesting phenomenon was observed. Under identical conditions of reduction with hydrogen (temperature, time, amount of hydrogen), nickelous oxide was most readily reduced to nickel in the catalysts NiO/ZnO and NiO/Fe₂O₃; it was most difficult to reduce when in admixture with MgO. This fact is evidently to be explained by the formation of stable compounds of difficultly reducible nickelous oxide with the metal oxides applied as carriers. A similar fact was observed by Hill and Selwood [5], who were unable to reduce NiO/MgO and NiO/TiO₂ to Ni/MgO and Ni/TiO₂. They attributed their lack of success to the tendency of nickel ions to build themselves into the lattice of the carrier.

It follows from this short review and from the results of our experiments that to obtain active, stable nickel catalysts, they must be prepared with a relatively low nickel content (15-20%) and ZnO or Al₂O₃ must be used as carrier.

EXPERIMENTAL

Preparation of Catalysts. All the catalysts studied were prepared by the coprecipitation of molar solutions of the nitrates of the corresponding metals with a 30% solution of caustic soda. The hydroxides formed were washed with pure tap water to free from NO_3^- ions, filtered off, dried at 120-130°, ground to a powder, and converted into tablets of cylindrical form (diameter, 3-4 mm; length, 5-6 mm) in a special press.

Experimental Procedure. The experiments on the hydrogenation and dehydrogenation of hydrocarbons were carried out in the usual continuous-flow apparatus, as previously described [6]. In all of the experiments the volume of reduced catalyst was 50 ml. The reduction of the catalyst was carried out in a stream of electrolytic hydrogen with gradual elevation of the temperature to 350-360°. In the reduction process, readings were made of the time and amount of hydrogen used. The nickel contents of the catalysts were determined by dissolving the catalyst in nitric acid, neutralizing the solution with ammonia until slightly alkaline, and precipitating with dimethylglyoxime.

The rate of passing cyclohexane vapor was 0.3 liter per liter of catalyst per hour; the rate for benzene was 0.06 liter per liter of catalyst per hour. Analysis of the issuing gas was performed in an Orsat—Lunge apparatus. The degree of conversion of cyclohexane into benzene, and of benzene into cyclohexane, was determined refractometrically [7].

Properties of Starting Materials. The cyclohexane used in the experiments had the following constants: b.p. 80°/760 mm, n_D 1.4264 and d^{4} 0.7780. The benzene (thiophene-free) had b.p. 80.0°/754 mm, n_D^{23} 1.5005 and d^{4} 0.8782.

Activity and Stability of the Nickel Catalysts Studied in Hydrogenation and Dehydrogenation Reactions. The initial dehydrogenation and hydrogenation activities of the catalysts investigated are given in Table 1. It will be seen from the results given in this table that nickel catalysts precipitated on Al_2O_3 and on ZnO have high dehydrogenating power. Catalysts precipitated on Cr_2O_3 and on MgO are of lower activity; and nickel on Fe_2O_3 is practically worthless as a dehydrogenation catalyst. All the samples studied, with the exception of Ni/Fe_2O_3, completely hydrogenate benzene to cyclohexane in one passage at 160-170°.

TABLE 1

Initial Hydrogenation and Dehydrogenation Activities of Nickel Catalysts on Various Carriers

Catalyst No.	Composition of catalyst	Cyclohexane		Benzene	
		n_D^{20} of catalyzate	% conversion	n_D^{20} of catalyzate	% conversion
1	14.4 Ni + 85.6 Al_2O_3	1.4158	74	1.4265	100
2	11.3 Ni + 88.7 ZnO	1.4790	78	1.4265	100
3	12.6 Ni + 87.4 Cr_2O_3	1.4570	51	1.4320	89.2
4	16.2 Ni + 83.8 MgO	1.4530	45	1.4265	100
5	16.9 Ni + 83.1 Fe_2O_3	1.4320	11	1.4950	6.6
6	19.5 Ni + 80.5 Al_2O_3	1.4870	87	1.4264	100
7	18.1 Ni + 81.9 ZnO	1.4830	82	1.4268	100
8	17.0 Ni + 83.0 Cr_2O_3	1.4725	70	1.4265	100
9	22.0 Ni + 78.0 MgO	1.4670	63	1.4260	100
10	21.1 Ni + 78.9 Fe_2O_3	1.4352	18	1.4948	6.8

With the object of determining the stabilities of the catalysts after functioning for a long period following the measurement of their initial activities, cyclohexane was passed, and then benzene, under the given conditions. The variation in hydrogenation and dehydrogenation properties of the catalysts studied are given in Figures 1, 2a and 2b. As will be seen from Fig. 1, the hydrogenating power of an Ni/Al_2O_3 catalyst remained quite unchanged after 80 hours. During the same period, the activities of Ni/ZnO and Ni/Cr_2O_3 catalysts fell by 18 and 20% respectively. The degree of dehydrogenation of cyclohexane fell gradually with time. The relatively high stabilities of the catalysts we have studied in hydrogenation and dehydrogenation reactions are evidently to be explained by the comparatively low concentration of finely dispersed nickel on the highly developed surface of the carriers. In this case the active nickel is distributed on the carrier in such a way that its splitting power is considerably weakened in comparison with that of the highly concentrated forms of nickel catalysts described in the investigations cited [1,3].
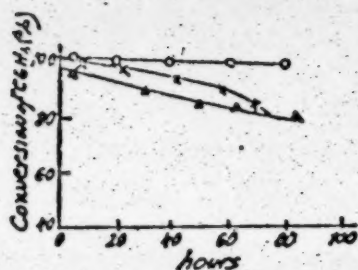
Fig. 1. Variation of hydrogenation properties of catalysts with time:
o — 19.5% Ni + 80.5% Al₂O₃;
x — 18.1% Ni + 81.9% ZnO;
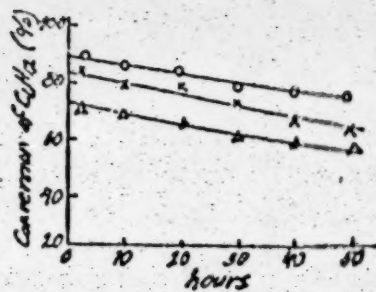Δ — 17.0% Ni + 83.0% Cr₂O₃

Fig. 2 A. Variation of dehydrogenation properties of catalysts with time:
o — 19.5% Ni + 80.5% Al₂O₃;
x — 18.1% Ni + 81.9% ZnO;
Δ — 17.0% Ni + 83.0% Cr₂O₃

Fig. 2B. Variation of dehydrogenation properties of catalysts with time:
o — 14.4% Ni + 85.6% Al₂O₃;
x — 11.5% Ni + 85.6% ZnO;
Δ — 12.6% Ni + 87.4% Cr₂O₃

Specially designed experiments showed that, right up to 350°, the catalyst that we have studied did not cause methane breakdown of cyclohexane; only above 350° did the splitting effect of these catalysts become appreciable. The experimental results obtained are given in Table 2. As will be seen from these results, only at 370° and higher do the catalysts studied have appreciable splitting action on hydrocarbons. The amounts of saturated hydrocarbons formed indicate that the carrier also has a definite effect on the extent of the decomposition of cyclohexane.

TABLE 2

Effect of Temperature on the Breakdown of Cyclohexane in Presence of Nickel Catalysts on Various Carriers

Temperature of Expt. (°C)	Composition of catalyst (%)					
	19.5% Ni + 80.5% Al₂O₃		18.1% Ni + 81.9% ZnO		17.0% Ni + 83.0% Cr₂O₃	
	H₂ (%)	Saturated hydrocarbons (%)	H₂ (%)	Saturated hydrocarbons (%)	H₂ (%)	Saturated hydrocarbons (%)
300	100	0	100	0	100	0
325	100	0	100	0	100	0
350	100	0	100	0	100	0
375	89	11	85.1	14.9	81.1	18.9
400	—	—	—	—	78	22.0

SUMMARY

1. A study has been made of the dependence of the hydrogenating and dehydrogenating powers of a number of nickel catalysts on their contents of finely dispersed nickel and on the nature of the carriers.

2. It has been shown that the most active nickel catalysts are obtained when Al₂O₃, ZnO, or Cr₂O₃ is used as carrier; nickel on ferric oxide is of no value as a hydrogenation or dehydrogenation catalyst.

3. It has been established that catalysts on carriers having a nickel content of up to 20% do not split cyclohexane at temperatures below 350°.

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REACTIONS OF VINYL ETHERS
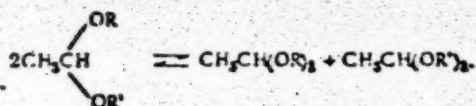
COMMUNICATION VIII. REACTIONS OF ACETALS DERIVED FROM ETHYLENE GLYCOL

### M. F. Shostakovsky, N. A. Gershtein, and Z. S. Volkova

It has already been noted in previous papers [1-3] that mixed acetals of the type $CH_3CH\begin{smallmatrix}OR\\OR'\end{smallmatrix}$ undergo partial

disproportionation when distilled:

$$2CH_3CH\begin{smallmatrix}OR\\OR'\end{smallmatrix} \rightleftharpoons CH_3CH(OR)_2 + CH_3CH(OR')_2 \; .$$

Acetals of ethylene glycol are particularly susceptible to such changes. Attempts to prepare hydroxy acetals by direct addition of alcohols to 2-vinyloxyethanol were not successful owing to the rapidity with which the vinyl ether undergoes cyclization, when heated, or in presence of acid catalyst.
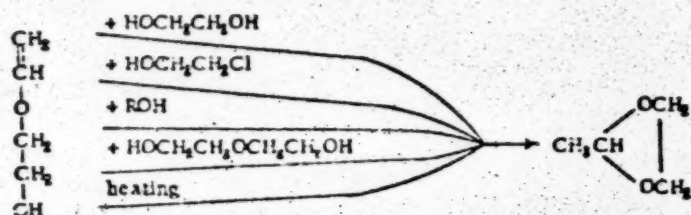
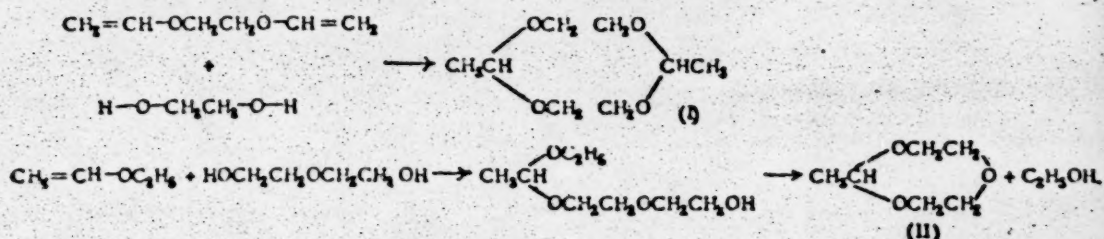Moreover, acetaldehyde ethyl 2-hydroxyethyl acetal, prepared by a different method [4], is also notable for its high instability, and shows a great tendency to react with formation of the same ethylene cyclic acetal (2-methyl-1,3-dioxolane):
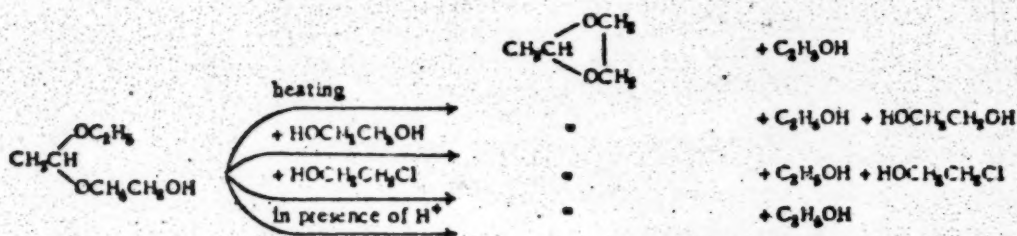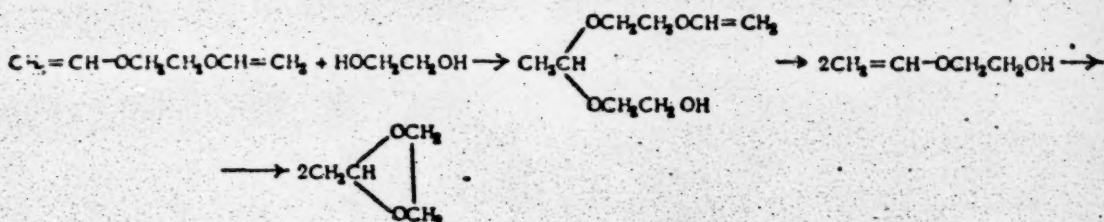

Even the diethyl ethylene diacetal (1,2-di(1-ethoxyethoxy)ethane), which has no free hydroxyl group, splits on being distilled at atmospheric pressure with formation of 2-methyl-1,3-dioxolane:
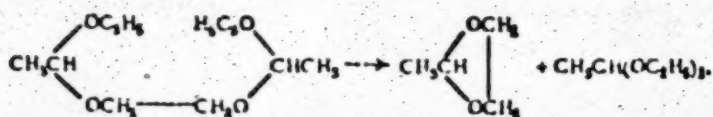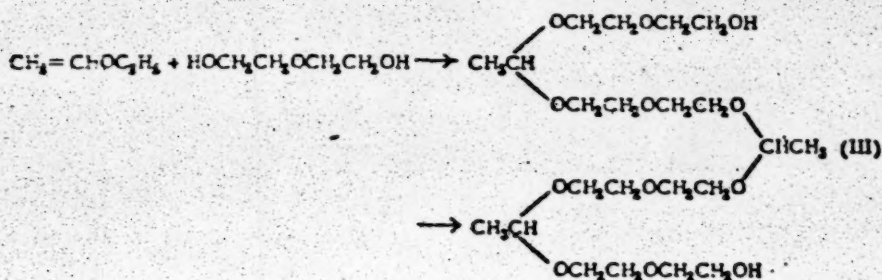
We have observed similar reactions when attempting to effect the synthesis of the cyclic diacetal (I) from ethylene glycol and the heterocyclic acetal (II) from diethylene glycol, in accordance with the following equations:

$$CH_2=CH-OCH_2CH_2O-CH=CH_2$$
$$+$$
$$H-O-CH_2CH_2-O-H \longrightarrow CH_3CH \begin{array}{c} OCH_2 \quad CH_2O \\ \\ OCH_2 \quad CH_2O \end{array} CHCH_3 \quad (I)$$

$$CH_2=CH-OC_2H_5 + HOCH_2CH_2OCH_2CH_2OH \longrightarrow CH_3CH \begin{array}{c} OC_2H_5 \\ \\ OCH_2CH_2OCH_2CH_2OH \end{array} \longrightarrow CH_3CH \begin{array}{c} OCH_2CH_2 \\ \\ OCH_2CH_2 \end{array} O + C_2H_5OH$$
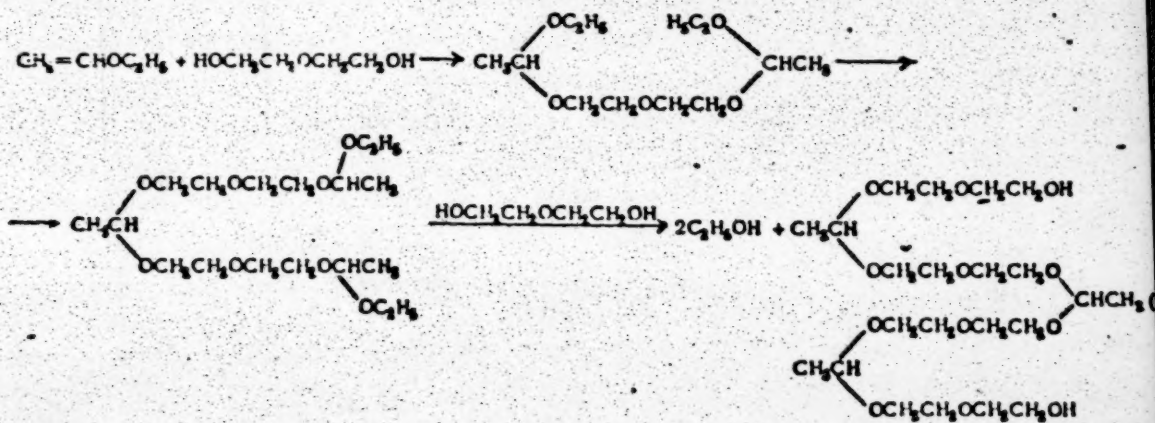$$(II)$$

However, in the first case, instead of the expected cyclic diacetal (I), the same 2-methyl-1,3-dioxolane was isolated in quantitative yield. The result obtained is to be explained by the decomposition, under the conditions of the reaction, of the 2-hydroxyethyl 2-vinyloxyethyl acetal formed, giving two molecules of 2-vinyloxyethanol, which then undergoes cyclization:

$$CH_2=CH-OCH_2CH_2OCH=CH_2 + HOCH_2CH_2OH \longrightarrow CH_3CH \begin{array}{c} OCH_2CH_2OCH=CH_2 \\ \\ OCH_2CH_2OH \end{array} \longrightarrow 2CH_2=CH-OCH_2CH_2OH \longrightarrow$$

$$\longrightarrow 2CH_3CH \begin{array}{c} OCH_2 \\ \\ OCH_2 \end{array}$$

Similarly, in the second case (synthesis of the heterocyclic acetal (II)), we obtained completely unexpected results, a 90% yield of a dihydroxy polyacetal derived from diethylene glycol being obtained:

$$CH_2=CHOC_2H_5 + HOCH_2CH_2OCH_2CH_2OH \longrightarrow CH_3CH \begin{array}{c} OCH_2CH_2OCH_2CH_2OH \\ \\ OCH_2CH_2OCH_2CH_2O \end{array} CHCH_3 \quad (III)$$

$$\longrightarrow CH_3CH \begin{array}{c} OCH_2CH_2OCH_2CH_2O \\ \\ OCH_2CH_2OCH_2CH_2OH \end{array}$$

It is evident that here we have again encountered a series of readily occurring reactions, which, we think, may be schematically represented as follows:

$$CH_2=CHOC_2H_5 + HOCH_2CH_2OCH_2CH_2OH \longrightarrow CH_3CH \begin{array}{c} OC_2H_5 \quad H_5C_2O \\ \\ OCH_2CH_2OCH_2CH_2O \end{array} CHCH_3 \longrightarrow$$

$$\longrightarrow CH_3CH \begin{array}{c} OCH_2CH_2OCH_2CH_2OCHCH_3 \\ \\ OCH_2CH_2OCH_2CH_2OCHCH_3 \end{array} \begin{array}{c} OC_2H_5 \\ \\ OC_2H_5 \end{array} \xrightarrow{HOCH_2CH_2OCH_2CH_2OH} 2C_2H_5OH + CH_3CH \begin{array}{c} OCH_2CH_2OCH_2CH_2OH \\ \\ OCH_2CH_2OCH_2CH_2O \end{array} CHCH_3$$
$$CH_3CH \begin{array}{c} OCH_2CH_2OCH_2CH_2O \\ \\ OCH_2CH_2OCH_2CH_2OH \end{array}$$

It is relevant here to point out that symmetrical acetals also readily undergo various reactions similar to those of compounds having multiple bonds [5 10]. The reactivity of acetals is related to their property of readily breaking down with formation of vinyl ethers as intermediate compounds; we have previously drawn attention to this fact [1, 2, 11]. We shall not consider the mechanism of these reactions in detail here, since we shall publish a special communication on this question.

EXPERIMENTAL

### 1. Reaction of 2-Vinyloxyethanol with Ethylene Glycol

The reaction was carried out in a three-necked flask fitted with reflux condenser, mercury-sealed mechanical stirrer, thermometer, and dropping funnel. Ethylene glycol (28 g, i.e. 0.45 mole), containing one drop of 33% hydrochloric acid, was added to chemically pure 2-vinyloxyethanol (b.p. 139.9°, n_D^{73} 1.4360; 39.0 g, i.e. 0.44 mole). Addition of the first drops of ethylene glycol was accompanied by an immediate rise in temperature from that of the room to 100°. Addition of ethylene glycol was discontinued until the reaction mixture had been cooled to 30°, when the remaining ethylene glycol was added; this further addition of ethylene glycol and catalyst did not, however, result in a further exothermic effect. The reaction mixture was set aside overnight and then fractionally distilled in a stream of nitrogen, yielding:

Fraction I, b.p. 65-68° at 758 mm; 2.8 g
Fraction II, b.p. 82.3-84° at 758 mm; 32.8 g
Fraction III, b.p. 84-186° at 758 mm; 2.3 g
Fraction IV, b.p. 74-75° at 3 mm; 26.4 g.

Fraction II, after treatment with sodium, yielded 31.9 g (82%) of the cyclic acetal 2-methyl-1,3-dioxolane, b.p. 82.6-82.9° at 762 mm; n_D^{18} 1.3981; d_D^{18} 0.9822; found MR_D 21.42; calculated for $C_4H_8O_2$ MR_D 21.758. The literature [12] gives b.p. 82.5; d^4 1.002.

Hydrolysis with 2% sulfuric acid and estimation of the acetaldehyde formed with sodium bisulfite indicated a $C_4H_8O_2$ content of 98.53% and 100.1% of that required theoretically. Fraction (IV) was found to be ethylene glycol: b.p. 196-197° at 760 mm, n_D^{18} 1.4320; yield 94%.

Under these reaction conditions 2-vinyloxyethanol isomerizes:
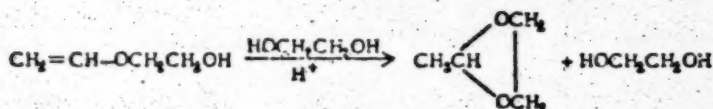
2. Reaction of Acetaldehyde Ethyl 2-Hydroxyethyl Acetal with Ethylene Glycol

An equimolecular mixture of 34 g of the ethyl 2-hydroxy acetal (b.p. 59.2°/2.5 mm, n_D^{18} 1.4180; d_4^{19} 0.9753) and 16 g of ethylene glycol (b.p. 196-197°, n_D^{18} 1.4320) was heated in a rotating stainless-steel 500 ml autoclave for 10.5 hours at 200-220°. The pressure in the autoclave attained 12-14 atm. The product (43.07 g) was a homogeneous, light-yellow, mobile liquid, from which two fractions were isolated:

Fraction I, b.p. 73-74°, 23.9 g; $n_D^{18.8}$ 1.3829.
Fraction II, b.p. 123-123.2° at 50 mm; 16.11 g; $n_D^{18.9}$ 1.4318

Fraction (I) was a mixture of the cyclic acetal and ethanol. It was not found possible to resolve this mixture with the aid of a column of 40 theoretical plates and a reflux index of 7, and the whole mass came over at 72.6-73.2° and had n_D^{18} 1.3830. By treating this fraction with sodium we succeeded in obtaining 2-methyl-1,3-dioxolane having the following constants: b.p. 82 7-83°; n_D^{18} 1.3982. Fraction (II) was unchanged ethylene glycol. It appears, therefore, that acetaldehyde ethyl 2-hydroxyethyl acetal reacts similarly to 2-vinyloxyethanol:
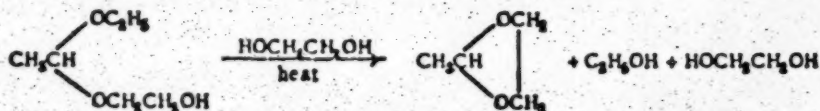
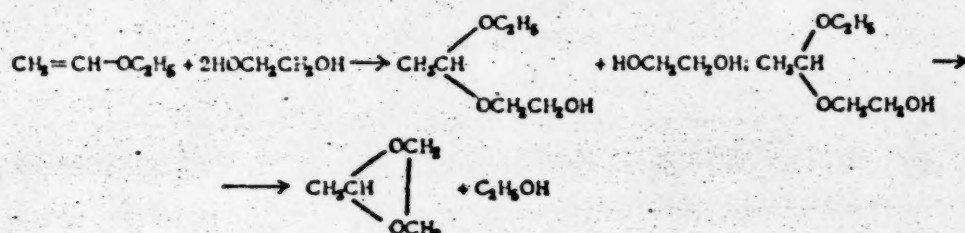### 3. Reaction between Ethyl Vinyl Ether and Ethylene Glycol in the Molar Ratio of 1:2

The reaction was carried out in an autoclave (150-180°, 8-10 atm, 12 hr, 30 min). Ethylene glycol (124 g, i.e. 2 moles) and ethyl vinyl ether (70 g, i.e. 1 mole) yielded a liquid (189.1 g), which gave on fractionation:

Fraction I, b.p. 52-75° (mainly 74-75°; 100.55 g; $n_D^{13.4}$ 1.3820

Fraction II, b.p. 113-115° at 31 mm; 67.75 g; n_D^{13} 1.4310

Trapped in coil at −14-15°   12.70 g; n_D^{13} 1.3830

Fraction (I) and the contents of the coil were treated together several times with sodium, yielding 60.2 g (70%) of 2-methyl-1,3-dioxolane, b.p. 82.5-83.2°, n_D^{20} 1.3982. Fraction (II) corresponded to ethylene glycol (54% of original), b.p. 195-196°, n_D^{14} 1.4320. The result of the reaction can be expressed by the following scheme:

$$CH_2=CH-OC_2H_5 + 2HOCH_2CH_2OH \longrightarrow CH_3CH \begin{array}{c} OC_2H_5 \\ OCH_2CH_2OH \end{array} + HOCH_2CH_2OH; \ CH_3CH \begin{array}{c} OC_2H_5 \\ OCH_2CH_2OH \end{array} \longrightarrow$$

$$\longrightarrow CH_3CH \begin{array}{c} OCH_2 \\ | \\ OCH_2 \end{array} + C_2H_5OH$$
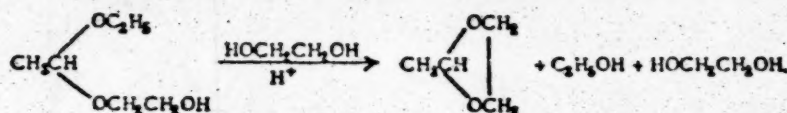
4. Reaction of Acetaldehyde Ethyl 2-Hydroxyethyl Acetal with Ethylene Glycol in Presence of Catalysts

The conditions were the same as in Experiment 1. The first drops of ethylene glycol containing catalyst produced an exothermic effect: the temperature rose rapidly to 85°. From 34 g of the ethyl 2-hydroxyethyl acetal and 16.1 g of ethylene glycol in presence of 0.025 g of concentrated hydrochloric acid, there were obtained:

Fraction I, b.p. 48-74° (mainly 73-74°); 29.8 g. n_D^{20} 1.3828
Fraction II, b.p. 73.5-74° at 3 mm; 16.11 g; n_D^{20} 1.4318

Fraction (I) yielded 15 g (67%) of 2-methyl-1,3-dioxolane, b.p. 81.8-82.2°, n_D^{20} 1.3830. Fraction (II) was ethylene glycol. In this case also the rate of the conversion of the ethyl 2-hydroxyethyl acetal into the cyclic acetal is considerably higher than that of the addition reaction, resulting in the isolation of the cyclic acetal:

$$CH_3CH \begin{array}{c} OC_2H_5 \\ OCH_2CH_2OH \end{array} \xrightarrow[H^+]{HOCH_2CH_2OH} CH_3CH \begin{array}{c} OCH_2 \\ | \\ OCH_2 \end{array} + C_2H_5OH + HOCH_2CH_2OH$$

5. Transformation of Acetaldehyde Ethyl 2-Hydroxyethyl Acetal under the Action of Heat
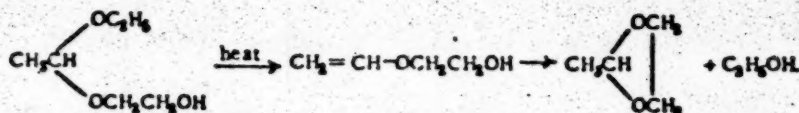
Pure acetaldehyde ethyl 2-hydroxyethyl acetal (34 g) was heated in a stainless steel autoclave for 8 hours at 200-215°; the pressure rose to 15-16 atm. At the end of the reaction 30.1 g of liquid was obtained; it gave the following results on being fractionated:

Fraction I, b.p. 52-73°; 4.22 g; n_D^{21} 1.3828
Fraction II, b.p. 73-74°; 27.30 g; n_D^{21} 1.3830
Residue   1.50 g

These results show that simple heating of the ethyl 2-hydroxyethyl acetal leads to its breakdown and to cyclization:

$$CH_3CH \begin{array}{c} OC_2H_5 \\ OCH_2CH_2OH \end{array} \xrightarrow{heat} CH_2=CH-OCH_2CH_2OH \longrightarrow CH_3CH \begin{array}{c} OCH_2 \\ | \\ OCH_2 \end{array} + C_2H_5OH$$

Attempts were made also to prepare the bis(2-hydroxyethyl) acetal and study its reactions.

6. Hydrolysis of Acetaldehyde Bis(2-chloroethyl) Acetal with Sodium Carbonate Solution
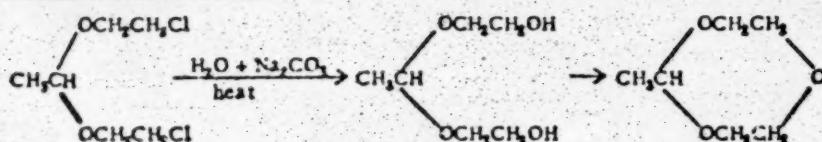
The reaction was carried out under the conditions employed for the hydrolysis of 2-chloroethanol in the synthesis of ethylene glycol [13]. The bis(2-chloroethyl) acetal was prepared by the disproportionation of the butyl 2-chloroethyl acetal, which occurs in the course of its synthesis:
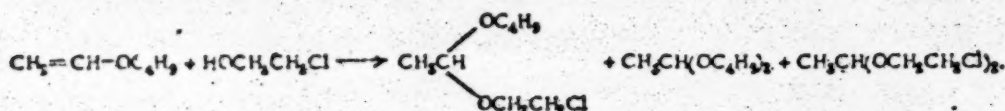
The bis(2-chloroethyl) acetal (b.p. 104-105° at 10 mm; d_4^{20} 1.1737; n_D^{20} 1.4529; (47.0 g), Na_2CO_3 (30.0 g), and water (200 ml) were heated in a rotating stainless-steel 500 ml autoclave for 4 hrs 25 min at 140-155° and for 5 hours at 180-190°. Gaseous products (965 ml) were collected, and a clear green liquid smelling of burnt sugar was obtained (259.7 g). The composition of the gaseous products was determined by analysis in an ORS apparatus.

Content of:

air by O_2 . . . . .28%
CO_2 . . . . 0%
unsaturated cpd. 0.4%
CO 9.8%
H_2 . . . . 34.0%
saturated cpd. (by diff.) . . 27.8%
   100%

The yield of pure sodium chloride was 26.5 g (89%).

The liquid part was treated as follows. A black resin, which we did not study further, was isolated from the ether extracts. There were no traces of free acetaldehyde present. After numerous fractionations of the aqueous part, in the course of which NaCl separated, 8.15 g of pure ethylene glycol, b.p. 78-79° at 8 mm; n_D^{20} 1.4318, was isolated.

A further experiment on the hydrolysis of the bis(2-chloroethyl) acetal under milder conditions (120-140° for 2 hours and 160-170° for 1 hr 25 min) gave similar results: from 29.7 g of the bis(2-chloroethyl) acetal, 20 g of Na_2CO_3, and 140 ml of water, 6.2 g of ethylene glycol, 550 ml of gaseous products, and some resinous substances were obtained. By the hydrolysis of the bis(2-chloroethyl) acetal, therefore, we did not succeed in obtaining the bis(dihydroxyethyl) acetal, because the reaction did not proceed in accordance with the scheme given above.

7. Reaction of 2-Vinyloxyethanol with Diethylene Glycol

The reaction was carried out in a three-necked flask, as in Experiment 1. One drop of concentrated hydrochloric acid was added to 27 g of diethylene glycol (b.p. 128.5-129° at 8 mm; n_D^{20} 1.4475), stirring was commenced, and 13 g of 2-vinyloxyethanol was added from a dropping funnel over a period of 1 hr 30 min. The reaction was exothermic, but the rise of temperature was slow (from 18° to 30°). The mixture was then set aside for 48 hours. Fractionation yielded 24.6 g (91.2%) of unchanged diethylene glycol, 18.5 g of 2-methyl-1,3-dioxolane (b.p. 81.5-82°; n_D^{20} 1.3982) and 3.07 g of a high-boiling substance having the consistency of glycerol: it decomposed when an attempt was made to distil it at 1.5 mm, and was therefore not studied further. The main reaction in this experiment may therefore be represented by the equation:
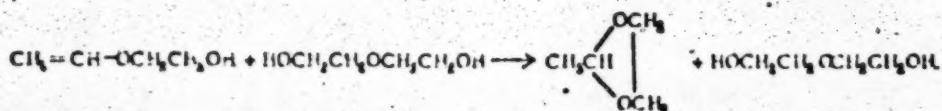
8. Reaction of Ethyl Vinyl Ether with Diethylene Glycol

The conditions employed were similar to those of the previous experiment. Ethyl vinyl ether (18 g) was added over a period of 1 hr 10 min to diethylene glycol (26.5 g), which had been carefully mixed with catalyst (HCl). The temperature rose from 16° to 55°. When the whole of the ethyl vinyl ether had been added, stirring was continued for 2.5-3 hours further, after which the reaction mixture was set aside overnight. Vacuum fractionation in a stream of nitrogen yielded:

Fraction I, b.p. to 50° at 3 mm: 12.36 g; n_D^{20} 1.3850

Fraction II, b.p. 58-250° at 3-10 mm (with incipient decomposition): 3.92 g

Residue in flask 23.23 g; n_D^{20} 1.4520

Distillation of Fraction (I) under ordinary pressure yielded 7.85 g of a substance boiling at 75-78° (mainly 78°) (this, after being distilled over $KMnO_4$ + KOH, was found to be ethanol, b.p. 78°, n_D^{20} 1.3618), and 3.2 g of acetaldehyde diethyl acetal, b.p. 103-104° at 758 mm; n_D^{20} 1.3820. An attempt to distil the residue in a high vacuum (0.17-0.19 mm) gave no positive results, since the product began to decompose.

A second experiment was performed under the same conditions with the object of isolating the high-boiling product, taking steps to prevent its partial decomposition. With this in view, at the end of the reaction the low-boiling products were driven off under reduced pressure at temperatures of up to 120°; the residue, after cooling, was extracted several times with absolute ether in order to remove low-boiling compounds and other substances soluble in ether, the bulk of the product being insoluble in ether. Residual ether was removed by treatment in the cold at low pressure with a stream of dry nitrogen that had been passed through alkaline pyrogallol solution, sulfuric acid, and caustic alkali. The low-pressure treatment was continued until constant weight was attained. The product was an almost colorless substance (28 g. i.e. 89.24% on the assumption that the product was the substance (III)); it had the consistency of glycerol, was without odor, and was insoluble in ether, but readily soluble in alcohol and water: c_4^{20} 1.1087; d_4^{20} 1.1067; n_D^{20} 1.4600. M (cryoscopic in benzene) found 554.5; 533.7; 541.

$$\text{Found \%: C 53.43; 53.50; H 9.38; 9.49}$$
$$\text{Calculated \%: C 52.59; \qquad H 9.16}$$

These results indicate the empirical formula to be $C_{22}H_{46}O_{12}$, the calculated value of M being 502.6. On the basis of this formula, the value found for MR_D is 124.2; MR_D calculated for $C_{22}H_{46}O_{12}$ is 123.276.

Hydrolysis with 2% sulfuric acid gave values of 100.9% and 101.1% $C_{22}H_{46}O_{12}$. These results permit us to ascribe the structure (III) to the product isolated.

9. Reaction of 1,2-Divinyloxyethane with Ethylene Glycol

The object of this experiment was to synthesize the substance (I). The reaction was carried out in a three-necked flask, as in the preceding experiments. Ethylene glycol (15.5 g) containing catalyst was added over a period of 15 minutes to 28 g of 1,2-divinyloxyethane having b.p. 126.8°, n_D^{20} 1.4350; d_4^{20} 0.9220. The temperature in the flask rose from 19° to 77°. When addition of ethylene glycol was complete, stirring was continued for 3.5 hours, and the reaction mixture was then set aside overnight. Vacuum distillation yielded 38.6 g (87.7%) of the cyclic acetal 2-methyl-1,3-dioxolane, b.p. 18.5°/2 mm. After redistillation under atmospheric pressure its constants were: b.p. 82°; n_D^{20} 1.3983; d_4^{20} 0.9798; found MR_D 21.67; calculated for $C_4H_8O_2$ MR_D 21.758.

SUMMARY

1. A study has been made of the reactions of 2-vinyloxyethanol, 1,2-divinyloxyethane, ethyl vinyl ether, and acetaldehyde ethyl 2-hydroxyethyl acetal with ethylene glycol and with diethylene glycol, when heated, and also in presence of catalysts (concentrated HCl).

2. It has been shown that both 2-vinyloxyethanol and the ethyl 2-hydroxyethyl acetal are extremely readily converted into the cyclic acetal 2-methyl-1,3-dioxolane. The second of these reactions proceeds via 2-vinyloxyethanol, which is cyclized under the conditions of reaction.

3. It has been shown that it is possible to apply the disproportionation reaction to the synthesis of high-molecular-weight acetals.

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* See Consultants Bureau English translation, page 617 ff.
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ACTIVATION OF VINYLCAPROLATCTAM IN PRESENCE OF HYDROGEN PEROXIDE

M. F. Shostakovsky and F. P. Sidelkovskaya

One of us [1, 2] has previously suggested that polymerization processes of unsaturated compounds do not constitute an isolated phenomenon, but are very closely associated with other chemical reactions of the original monomers. Air, solvents, and other substances present during polymerization may have important effects [3]. These factors may either encourage the formation of high-polymer products, or, on the contrary, involve the original compounds in other reactions (hydrolysis, alcoholysis, oxidation) and so lower the yield of polymer. The temperature and the concentration and amount of catalyst are also of importance. It has been shown, in the case of vinyl acetate, that the same catalysts (hydrogen peroxide, benzoyl peroxide) not only cause polymerization, but also facilitate addition of alcohols, acids, and water [2].

In a study of the polymerization of vinylcaprolactam in presence of 30% hydrogen peroxide [4] it was found that at 140-150° only polymer formation occured. At 100-125°,, however, not only polymers, but also small amounts of monomeric compounds, caprolactam and acetaldehyde, were found in the reaction products. Their formation may be explained by hydrolysis of the original vinylcaprolactam. As there is very little information in the literature on the question of hydrolysis in presence of peroxides [2]. It was considered that a more detailed investigation of this reaction would be of great interest.

In this investigation a study has been made of the reaction of vinylcaprolactam (2-oxo-1-vinylhexamethylenimine) with water in presence of hydrogen peroxide. Actually, in this case two processes proceed simultaneously, namely hydrolysis (I) and polymerization (II):
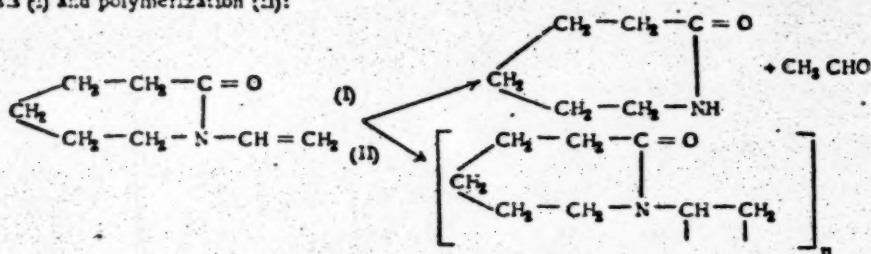
According to the temperature and ratio of the components, one or other reaction predominates. In a control experiment, in which vinylcaprolactam was heated with water at 100° in absence of hydrogen peroxide, neither polymerization nor hydrolysis products were obtained in detectable amounts: the vinylcaprolactam was recovered unchanged practically completely. It follows that hydrogen peroxide is a catalyst both for the polymerization and for the hydrolysis of vinylcaprolactam. The results of the experiments are given in Tables 1 and 2. It follows from Table 1 that with increase in dilution at constant temperature the percent hydrolysis rises and the percent polymerization falls. On the other hand, at a given dilution (Table 2), with rise in temperature the percent polymerization rises.

TABLE 1

Reaction of Vinylcaprolactam with Water in Presence of H_2O_2 at Constant Temperature and Varying Ratio of Components

Expt. No.	Molar ratio of vinyl-caprolactam and water	Temp. of outer bath (°C)	Temp. of reaction mixture (°C)	Yield of polymer (%)	Yield of caprolactam (%)	Total per-cent con-version
1	1:10	120 — 130	97 — 98	19.5	64	83.5
4	1:15	120 — 135	97 — 99	15.3	75	90.3
9	1:135	120 — 135	97 — 99	7.5	84.5	92.0

Temperature intervals in the range 60 - 100° were investigated. It was not found possible to raise the temperature above 100°, since already at this temperature vigorous boiling of the mass was to be observed. The amount of catalyst and the duration of the experiment were the same in all cases (see Experimental).

TABLE 2

Reaction of Vinylcaprolactam with Water in Presence of H₂O₂ at Constant Ratio of Components and Varying Temperatures

Expt. No.	Molar ratio of vinylcaprolactam and water	Temp. of outer bath (°C)	Temp. of reaction mixture (°C)	Yield of polymer (%)	Yield of caprolactam (%)	Total percent conversion
12	1:135	79 — 82	60 — 62	Traces	Traces	Practically 0
11	1:135	100 — 105	79 — 82	6	40	46
9	1:135	120 — 135	97 — 99	7.5	84.5	92.0
10	1:135	150 — 160	100	38.9	55.2	94.1

It should be noted that below 100° the general reactivity of vinylcaprolactam in presence of H₂O₂ falls (Experiments nos. 11 and 12, Table 2). By variation of temperature and dilution, therefore, the process may be directed either toward predominant hydrolysis, or toward polymerization.

These experiments confirm the conclusion reached previously [1, 2, 3] that the polymerization of unsaturated compounds, leading to the formation of macromolecular products, is only a special case of the reaction of addition of one organic compound to another. Hence, the course of polymerization processes (particularly in solution) is analogous to that of other addition reactions, being determined both by the nature of the original monomer, and by the nature of the medium and by the physical conditions under which the process is conducted (temperature, light, pressure, catalyst, concentration).

EXPERIMENTAL

Reaction of Vinylcaprolactam with Water in Presence of Hydrogen Peroxide

Vinylcaprolactam (15.9 g) and distilled water (20 ml) were introduced into a three-necked flask fitted with stirrer, thermometer, and reflux condenser attached to three Tishchenko vessels filled with water, and heated in an oil bath. With the temperature of the oil at 120-125° and that of the reaction mixture at 97-98°, small amounts of 28% hydrogen peroxide were added every 1.5-2 hours, the total amount added being 0.51 g, and the duration of the experiment being four hours. Heating was discontinued, nitrogen was blown through the system, and the product was treated as follows: the amount of acetaldehyde was determined by titrating an aliquot part of the reaction mixture and also the contents of the Tishchenko vessels with sodium bisulfite, the calculation being carried out by the formula:

$$A = \frac{2.2 (B - C)D}{1000E}$$

(A is the amount of acetaldehyde (g), B is the amount of 0.1 N iodine (ml) consumed in a control experiment, C is the amount of 0.1 N iodine (ml) consumed in the working experiment, D is the total amount of solution to be analyzed (ml), and E is the volume of solution taken for analysis (ml)).

As a result of the titration it was found that there was 1.15 g acetaldehyde in the main reaction product, and 0.44 g in the solution from the absorption vessels: 1.59 g of acetaldehyde in all. This amount of acetaldehyde corresponds to 5 g (32%) of the original vinylcaprolactam *.

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* In this and succeeding experiments, in spite of all precautions taken, it was not found possible to account for the whole of the acetaldehyde. It is evidently partly lost when the separate portions of catalyst are introduced into the reaction mixture. It is necessary to estimate the degree of hydrolysis by the amount of caprolactam isolated.

The main reaction product was fractionated, first at atmospheric pressure, and then under reduced pressure; the following fractions were obtained:

Fraction I, b.p.   40-95°/755 mm;   0.8 g

Fraction II, b.p.   29-40°/29 mm;   17.9 g; $n_D^{?}$ 1.3385

Fraction III, b.p. 117-120°/5 mm;   7.7 g; n_D 1.4760

Resinous residue;   4.35 g

Fraction I had the sharp odor of acetaldehyde; it was an aqueous solution of this substance: 0.4 g of Fraction I was added to a solution of 0.1 g of 2,4-dinitrophenylhydrazine in 5 ml of 10% hydrochloric acid, when orange crystals of the 2,4-dinitrophenylhydrazone of acetaldehyde (m.p. from alcohol, 162-163°, not depressed in admixture with authentic sample) came down. Fraction II consisted mainly of water. Fraction III readily crystallized out in the condenser; the crystals were transferred to a flask having a sword-shaped side tube and were distilled, yielding 7.3 g of caprolactam, m.p. 64-67° (68-69° after recrystallization from dry ether; the literature [5] gives 66-70°). In admixture with pure caprolactam there was no depression in melting point. The resinous residue (4.3 g) was dissolved in 10 ml of benzene and reprecipitated with 100 ml of diethyl ether. The product was 2 g of polyvinylcaprolactam in powder form. By fractionation of the benzene solution, a further 1 g of crystalline caprolactam (m.p. 66-68°) was isolated, and also a further 1 g of resinous polymer. As has already been shown [4] the latter was a mixture of pure polymer (in the form of powder) and monomer. In order to characterize the polyvinylcaprolactam, its specific viscosity η_{sp} and molecular weight were determined.

The specific viscosity η_{sp} (1 g of polymer in 100 ml of benzene) was 0.2079. The molecular weight, determined cryoscopically in benzene, varied over the range 3000-5000.

The remaining experiments on the polymerization of vinylcaprolactam in aqueous solution in presence of hydrogen peroxide, and also the treatment of the reaction products, were carried out by the procedure described above. The ratio of components and the temperature were varied. In all these experiments the time was four hours, the amount of hydrogen peroxide (28%) added was 0.52 g, and the amount of vinylcaprolactam taken was 10-12 g.

SUMMARY

The reaction of vinylcaprolactam with water in presence of hydrogen peroxide has been studied, and it has been shown that two processes occur: hydrolysis and polymerization. With rise in temperature and reduction in dilution the percent polymerization increases and the percent hydrolysis diminishes.

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DEPOLYMERIZATION OF DICYCLOPENTADIENE BY THE CONTINUOUS METHOD

N. F. Kononov, Z. Ya. Lapshina, and S. S. Novikov

In recent years a number of papers devoted to the search for means of utilizing cyclopentadiene for the preparation of various substances have appeared in the literature [1-3]. In this connection the problem of developing accessible and convenient methods for the preparation of this valuable hydrocarbon becomes of particular importance. It is well known that up to the present time the main source of cyclopentadiene has been its dimer, which is formed as a by-product of the coal-tar industry or by the pyrolysis of petroleum products [2].

In order to prepare cyclopentadiene from its dimer, the latter is generally depolymerized by heating at 175-180°, with simultaneous distillation of the monomer formed [3]. This method, in spite of its wide use, has a number of disadvantages. In the first place, it is inconvenient because of its low productivity (only 40-60 g of monomer is obtained per hour from one liter of reaction vessel space. Furthermore, in the intermittent method of preparing cyclopentadiene, part of the dimer, owing to the effect of prolonged heating, is converted into more complex polymers, and the yield of monomer is therefore reduced.

Raur and Frater [4] determined the equilibrium constants for the depolymerization process over the range 149-193°. Values of 277, 591, 742, 1177, and 2200 were found for the temperatures 149°, 165°, 170°, 180°, and 195° respectively. The rate of the unimolecular reaction for the decomposition of the dimer is higher in this temperature range than that of the bimolecular dimerization reaction, and decomposition proceeds practically to completion. The rate constant for the decomposition reaction in the liquid phase has been determined by Wasserman for temperatures in the range 79-150°.

$$k = 6 \cdot 10^{12} e^{-(34000/RT)}$$

In the temperature range cited above the heat of reaction for the decomposition has been found to be 12.3 kcal per mole [5].

On the basis of this information we carried out experiments with the object of developing a continuous method of decomposing the dimer. It was essential that the following conditions should be fulfilled: 1) a minimum period of contact of dimer with the heated surface; 2) rapid supply of heat to the reaction zone; 3) fractional condensation of dimer carried away by the vapor of the cyclopentadiene formed.

These requirements were satisfied by the apparatus represented in the figure. The apparatus consisted of a glass column 1, height 700 mm, diameter 30 mm, having a filling of short sections of glass tube, diameter 5 mm, average length 5 mm. The lower part of the column, height 500 mm, was the reactor, and was provided with a spiral winding for heating. The higher part of the column served as a fractionating column with air cooling. The dimer entered continuously, from the reservoir 3, through a perforated glass tube into the upper part of the reactor. The lower part of the column communicated with a vessel 2, which served for the decomposition of residues of dimer. Experiment showed that with suitable regulation of the supply of dimer the decomposition was generally complete in the column. In the upper part of the column the separation of entrained dimer from cyclopentadiene vapor took place. The vapor then passed further to a water-cooled condenser 4, and the condensed cyclopentadiene collected in the receiver 5, which was cooled with ice.

When the reaction conditions had been established, the apparatus continued to work for a day or so. The yield of monomer was 99 % of the dimer passed. The productivity of the reactor was 150 g per liter of reaction space.

Formation of higher polymers of cyclopentadiene occured only to a very slight extent; it nevertheless took place, and it was therefore necessary to stop the process periodically to free the apparatus from resins formed on the walls in a thin layer that hindered heat transfer. On the average a stop was made after 100-150 hours of continuous operation.

On very rare occasions, when the supply of dimer was increased (at 200° the supply was generally 50-60 ml per hour), it was not fully separated in the fractionation column and was drawn by monomer vapor into the condenser.
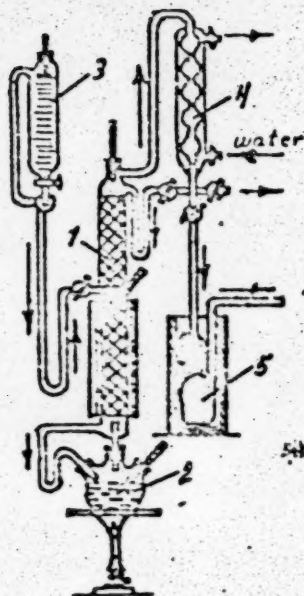
Apparatus: 1—column; 2—still flask;
3—measuring reservoir; 4—condenser;
5—receiver.

which was indicated by the thermometer and also by the change in the refractive index of the monomer. In such a case the supply of dimer was diminished, and the monomer, containing dimer impurity was directed into the fractionation column, from which it passed to the decomposition zone. When vapor of monomer free from dimer passed from the column, the supply of fresh dimer for decomposition was renewed.

As an example we will give the figures for a typical experiment, which lasted for 12 hours. For the decomposition 582.6 g of dimer was taken- it had the following constants: b. p 58 60° at 14 mm, n_D^{19} 1.5125; d_4^{21} 0.9712 calculated MR_D 40 84, found MR_D 40.56. The decomposition temperature was maintained in the range 195-200°. The product was 575.6 g of monomer having the following constants: b.p. 40-42°; n_D^{19} 1.4446; d_4^{19} 0.8016; calculated MR_D 22.16; found MR_D 21.87. Thus the undoubted advantages of the continuous method of preparing monomer over the intermittent method have been demonstrated, and a simple apparatus for carrying out the process has been proposed.

In conclusion the authors consider it to be their pleasant duty to express their thanks to N.L Shuikin for valuable advice in the course of the performance of this work.

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INVESTIGATION OF THE MECHANISM OF CYCLIZATION
# WITH THE AID OF DEUTERIUM

COMMUNICATION 1. CYCLIZATION OF 2-METHYL-1,5-HEXADIEN-3-ONE

D. N. Kursanov, Z. N. Parnes, I. I. Zaretskaya, and I. N. Nazarov

The investigations of Nazarov and coworkers have shown that substituted 1,5-hexadien-3-ones are readily cyclized in presence of acids, giving substituted cyclopentenones [1]:
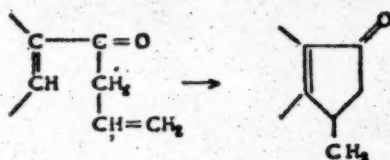
The In explanation of these reactions Nazarov proposed an ionic mechanism [2], according to which the reaction is intermolecular and commences with the addition of a hydrogen ion to the molecule of the ketone undergoing cyclization. This concept corresponds, for example, to Scheme 1, according to which the first stage of the process is the addition of a proton (in Scheme 1, a deuteron) at the terminal carbon of the allyl radical, with formation of a carbonium ion (a); this then cyclizes to give the cyclic ion b, which loses a proton with formation of 2,4-dimethyl-2-cyclopenten-1-one (in Scheme 1, 2-methyl-4-methyl-d-2-cyclopenten-1-one). Scheme 1 is as follows:
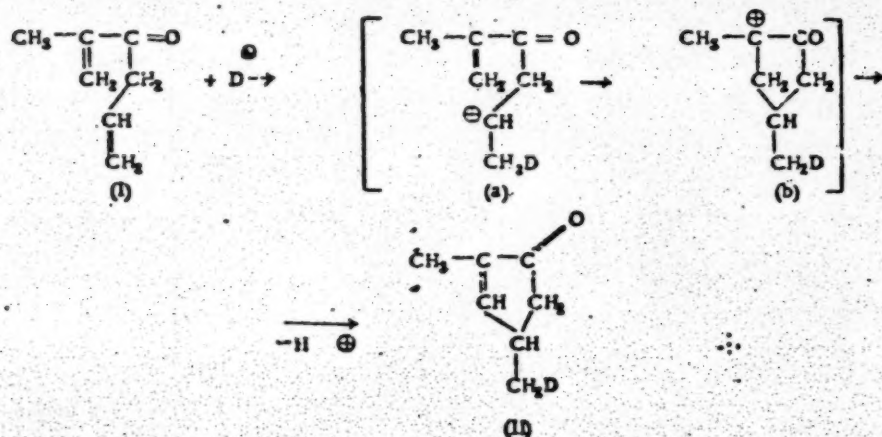
However, the possibility cannot yet be excluded that cyclization proceeds by intramolecular transfer of a transfer of a hydrogen atom (Scheme 2):
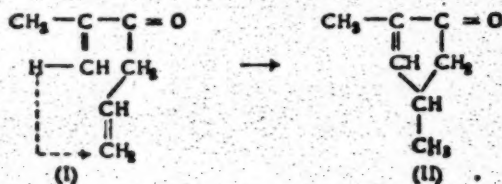
We hoped to prove the mechanism of this reaction by carrying out the cyclization in presence of deuterium-rich phosphoric acid. In that case, if the mechanism proposed by Nazarov were correct, then it follows from Scheme 1 that the dimethylcyclopentenone obtained would contain deuterium. This method of proof, however, is possible only when the original dienone (I) and the cyclic ketone II are unable, under the conditions of the experiment, to exchange their hydrogen atoms for deuterium, or when they exchange them so slowly that this exchange can be taken into account.

It is well known that, under suitable conditions, ketones in contact with deuterium oxide are unable to exchange hydrogen in the α-position to the carbonyl group for deuterium [3]. These exchange reactions are generally carried out in presence of alkaline catalysts, but cases are known also of the acid catalysis of these reactions [4]. Our first problem, therefore, was to investigate the tendency of the dimethylcyclopentenone II to undergo deuterium exchange under the conditions under which the cyclization of 2-methyl-1,5-hexadien-3-one (I) was performed. Our experiments showed that exchange of hydrogen atoms of the dimethylcyclopentenone for deuterium proceeds only extremely slowly (Table 1). We then carried out the cyclization, under the same conditions, of 2-methyl-1,5-hexadien-3-one (I) in presence of deuterium-rich phosphoric acid. It was found that the dimethylcyclopentenone obtained (II) contained considerably more deuterium than in the previous experiments (Table 2).

The results of these preliminary experiments were in agreement with the intermolecular ionic mechanism for the reaction (for example, that given in Scheme 1), but did not constitute a complete proof, since the possibility had not been excluded that the original 2-methyl-1,5-hexadien-3-one entered into an exchange reaction considerably more readily than the dimethylcyclopentenone, thus explaining the enhanced deuterium content of the cyclic ketone obtained.

In order to obtain a complete proof of the reaction mechanism it was necessary to study the tendency for the methylhexadienone to undergo exchange under the precise conditions of the cyclization reaction. For this purpose it was necessary to find conditions under which only part of the methylhexadienone would be converted into the dimethylcyclopentenone, i. e. under which the cyclization reaction would not proceed to completion. The recovered methylhexadienone and the dimethylcyclopentenone obtained would have to be examined for their deuterium contents. An excess of deuterium in the cyclic ketone could in this case be explained only by its introduction in the process of cyclization, and would thus form a convincing proof of the mechanism of this reaction. From the experimental side, however, this method of proof met with considerable difficulties: thus the boiling points of the ketones (I) and (II) differ only by 7.5° at 40 mm, and in order to separate them a highly efficient column working at a constant low pressure was required. Another difficulty was that of choosing conditions for incomplete cyclization (Table 3). After a number of experiments, however, these conditions were found. Incomplete-cyclization experiments in presence of deuterium-rich phosphoric acid showed, in the first place, that the methylhexadienone showed no appreciable tendency to undergo exchange under the cyclization conditions: the density excess of the water from the combustion of 2-methyl-1,5-hexadien-3-one in Experiment 9 was 15γ, and in Experiment 10 it was 32 γ. In the second place, it was found that the dimethylcyclopentenone formed in the course of incomplete cyclization was appreciably enriched in deuterium. In Experiment 10, for example, the combustion water of the dimethylcyclopentenone had a density excess of 190γ.

The results cited above show that the cyclization reaction is accompanied by introduction of deuterium from the deuterium-rich phosphoric acid into the cyclic ketone formed, thus confirming the reaction mechanism proposed by Nazarov. The enrichment in deuterium of the cyclic ketone was, however, less than that to be expected on the basis of the isotopic composition of the hydrogen of the phosphoric acid.

A probable explanation of this is that the dissociation constant of light phosphoric acid is higher than that of heavy phosphoric acid and, at the same time, the rate of the addition of a proton is higher than that of a deuteron. Another possible explanation is that the intermolecular mechanism of cyclization is to some extent accompanied by the intramolecular mechanism (Scheme 2). In order to solve this question we carried out the cyclization of 2-methyl-1,5-hexadien-3-one in presence of practically pure phosphoric acid-d. The cyclic ketone obtained under these conditions corresponded very closely in its isotopic composition to monodeuteriodimethylcyclopentenone, i. e. in this case practically exactly one atom of deuterium entered into the molecule of the cyclopentenone. It was thus shown that the intermolecular cyclization mechanism was the only one possible, and Nazarov's postulate of an ionic intermolecular mechanism for this reaction was thus confirmed.

It is possible to obtain more detailed information about the mechanism of this reaction by determining the position of the deuterium atom in the cyclic ketone.

EXPERIMENTAL

Investigation of Hydrogen Exchange in Dimethylcyclopentenone

Dimethylcyclopentenone was prepared by the cyclization of 2-methyl-1,5-hexadien-3-one and the corresponding methoxy ketones in presence of phosphoric acid, and after distillation through a column it had the following constants: b. p. 77.0 -77.5°/37 mm and n_D^{22} 1.4670. In the study of the deuterium exchange, the dimethylcyclopentenone was introduced into a two-necked flask together with an equal weight of phosphoric acid (sp. gr. 1.79) enriched in deuterium. At the end of the experiment the reaction mixture was poured into an aqueous solution of sodium bicarbonate, extracted with ether, dried with magnesium sulfate, and distilled from a small Favorsky flask. The main fraction had b.p. 46.0-42.0/10 mm and n_D^{15} 1.4673. The conditions and results of the experiments are given in Table 1.

TABLE 1

Expt. No.	Temp. (°C)	Time (hr)	Initial equiv. density excess of phosphoric acid (γ)	Calcd. density excess for exchange of 2H (γ)	Density excess found (γ)	Exchange (% of calcd. value)
1	24	24	25660	3905	775	20
2	19	20	25660	3985	650	16
3	20	2	8630	1020	31	3

From these experiments it will be seen that exchange between dimethylcyclopentenone and heavy phosphoric acid proceeds only very slowly. Under the conditions of Experiment 3 practically no exchange occurred.

Cyclization of 2-Methyl-5-hexadien-3-one in Presence of Heavy Phosphoric Acid

The 2-methyl-1,5-hexadien-3-one used in the experiment had b.p. 36-37°/21 mm and $n_D^{18.2}$ 1.4760. The cyclization was performed in presence of an equal weight of phosphoric acid (sp. gr. 1.79) having an equivalent density excess of 9040 γ. The results of the experiment are given in Table 2.

TABLE 2

Expt. No.	Temp. (°C)	Time (hr)	Calcd. density excess (γ) for the change of		Density excess found (γ)
			2H	1H	
4	19	20	4045	2260	2615

It will be seen that the cyclization product in this experiment is highly enriched in deuterium in comparison with those of Experiments 1-3.

Fractionation through a Column of a Mixture of 2-Methyl-1,5-hexadien-3-one and Dimethylcyclopentenone

In the preparation of 2-methyl-1,5-hexadien-3-one from the corresponding compounds by removal of methanol (heating with p-toluenesulfonic acid), partial cyclization into dimethylcyclopentenone occurs. Similar phenomena have been observed previously by Nazarov and coworkers in other cases [5]. For fractionation through a column we took the mixture of ketones obtained by splitting methanol from the methoxy compounds corresponding to 2-methyl-1,5-hexadien-3-one in presence of p-toluenesulfonic acid. We used a column made up of single turns of glass spirals having an efficiency at ordinary pressure of 25 theoretical plates and provided with a manostat. The fractionation curves clearly showed that it was possible to separate these ketones with the aid of this column. The amount of the ketone mixture taken for fractionation was 60 g. and the following fractions were obtained:

Fraction I, head fraction collected to 71.5° / 39 mm; $n_D^{18.2}$ 1.4690, weight 8.5 g.
Fraction II, 2-methyl-1,5-hexadien-3-one, b.p. 71.5°/39 mm; $n_D^{18.2}$ 1.4730; weight 18.2 g.
Fraction III, intermediate, $n_D^{18.2}$ 1.4690; weight 7.2 g.
Fraction IV, dimethylcyclopentenone, b.p. 79.4° at 39 mm; $n_D^{18.2}$ 1.4679; weight 6.7 g.
Fraction V, b.p. 79.5-87.1°, $n_D^{18.2}$ 1.4572, weight 1.8 g.
Residue, 14.0 g.

TABLE 3

Determination of the Conditions for the Incomplete Cyclization of 2-Methyl-1,5-hexadien-3-one.

Expt. no.	Sp. gr. of phosphoric acid	Temp. (C)	Time (hrs.)	Results of experiments
5	1.75	20	3	Cyclization did not go
6	1.798	22-23	3	Cyclization went completely
7	1.790	20	1	Cyclization did not go
8	1.798	20-21	1.7	Cyclization went to the extent of 50% (judging only from the refractive index)

The fractionation curve is given in Fig. 1.

Fraction II (2-methyl-1,5-hexadien-3-one) was redistilled through the same column. The main fraction had b.p. 72.0° at 42 mm; $n_D^{18.2}$ 1.4738, d_4^{18} 0.8897 (Fig. 2).

Fraction IV (dimethylcyclopentenone) was also redistilled through the column. The main fraction had b.p. 77.0-77.5° at 37 mm; $n_D^{17.5}$ 1.4670; d_4^{18} 0.9367.

Incomplete Cyclization of 2-Methyl-1,5-hexadien-3-one in Presence of Heavy Phosphoric Acid

Experiment 9. To stirred 2-methyl-1,5-hexadien-3-one (22.4 g) contained in a three-necked flask, phosphoric acid (21.3 g; sp.gr. 1.794) having an equivalent density excess of 8630 γ was added carefully; the flask was cooled with ice water, and the temperature did not exceed 7°. When addition of phosphoric acid was complete, the flask was placed in a thermostatic water bath, and the temperature in the flask was maintained within the range 20-21° for 1 hour 45 minutes. At the end of this period the reaction mixture was poured into a bicarbonate solution, and was then extracted with ether and dried with magnesium sulfate. After being distilled in order to remove resin, the mixture of reaction products was fractionated through a column. The amount taken for distillation through the column was 13.7 g and the following fractions were obtained:

Fraction I, b.p. 62.5-67.2° at 35 mm; 1.3 g
Fraction II, b.p. 67.2-67.5° at 35 mm; 4.2 g.

Fraction II was pure 2-methyl-1,5-hexadien-3-one, $n_D^{18.1}$ 1.4730. It was not found possible to distill the residue through the column. It was transferred to a small Favorsky flask and vacuum-distilled. The substance had an extended boiling range, 73-80°/35 mm; n_D^{18} 1.4705, and was evidently a mixture of 2-methyl-1,5-hexadien-3-one and dimethylcyclopentenone, in which, according to the refractive index, 45% of dimethyl-cyclopentanone was present.

The 2-methyl-1,5-hexadien-3-one was burnt, and the combustion water was purified by the method adopted in our laboratory [6]. The density excess of the combustion water was found to be 15 γ. The calculated density excess for an exchange of 2H was 1040 γ. The mixture of ketones (b.p. 73-80°/35 mm) was also burnt, and the resulting water had a density excess of 112 γ. By taking into consideration the percentage composition of the ketone mixture and also the fact that the 2-methyl-1,5-hexadien-3-one was only slightly enriched in deuterium, an approximate calculation of the density excess of the combustion water from the dimethylcyclopentenone present could be made; the value found was 215 γ.

Experiment 10. In this experiment 40.85 g of 2-methyl-1,5-hexadien-3-one and 37.90 g of phosphoric acid having a density excess of 8630 γ were taken. Addition of phosphoric acid was carried out as in the preceding experiment. In the course of the experiment the temperature varied from 18° to 20.5°, and the experiment lasted for 2 hours 25 minutes. The reaction mixture was then treated as in the preceding experiment. The residue after removal of ether was vacuum-distilled. It came over completely between 42° and 68° at 8 mm. The distillate was distilled through a column, and after the head fraction 15.2 g of 2-methyl-1,5-hexadien-3-one (I), b.p. 69.5-70°/36 mm and n_D^{18} 1.4737 was obtained. After a small intermediate fraction (0.8 g), 3.5 g of 2,4-dimethyl-2-cyclopenten-1-one (II), b.p. 75.2-76.5°/35-36 mm and $n_D^{18.6}$ was obtained.
The density excess of the combustion water from 2-methyl-1,5-hexadien-3-one was 32 γ. For exchange of 2H, the density excess should have been 1110 γ. The density excess of the combustion water from dimethylcyclopentenone was 190 γ.

Cyclization of 2-Methyl-1,5-hexadien-3-one in Presence of Phosphoric Acid-d_3

Experiment 11. Phosphoric acid-d_3 (sp. gr. 1.76; equivalent density excess 91,000 γ) was added gradually to 4.02 g of 2-methyl-1,5-hexadien-3-one. The reaction mixture remained at 20-21° for 3 hours 30 minutes. It

was treated as in the preceding experiments. The dimethylcyclopentenone obtained was distilled off from resin and distilled from a Favorsky flask (b p 45-46°/9 mm, n_D^{18} 1.4670). It may be considered from the constants that the cyclization reaction went to completion. The density excess of the combustion water from the ketone was 8290 γ. The value calculated for the exchange of one hydrogen atom was 7765 γ.

SUMMARY

1. It has been shown that 2,4 dimethyl 2-cyclopenten-1-one and 2-methyl-1,5-hexadien-3-one do not undergo appreciable protium deuterium exchange when placed in contact with heavy phosphoric acid for two hours at 20°.

2. It has been shown that in the cyclization of 2-methyl-1,5 hexadien 3 one in presence of heavy phosphoric acid (sp.gr. 1.79) at 20° the dimethylcyclopentenone obtained is appreciably enriched in deuterium.

3. It has been shown that in the cyclization of 2-methyl-1,5-hexadien-3-one in presence of pure phosphoric acid-d_3 a monodeuteriod methylcyclopentenone is obtained.

4. It follows from the experimental results obtained that the cyclization of 2-methyl-1,5 hexadien 3 one is accompanied by the introduction of one deuterium atom into the dimethylcyclopentenone molecule formed, and this constitutes a proof that the cyclization reaction has an intermolecular ionic mechanism, as proposed by Nazarov.

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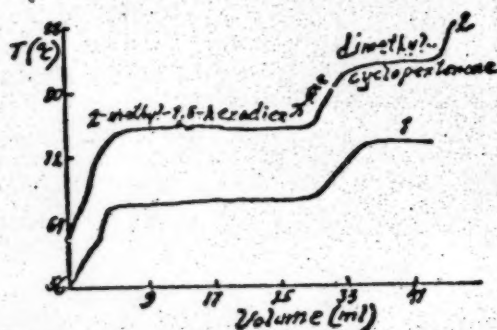
Fig. 1. Fractionation curves of a mixture of 2 methyl-1,5-hexadien-3-one and dimethylcyclopentenone:
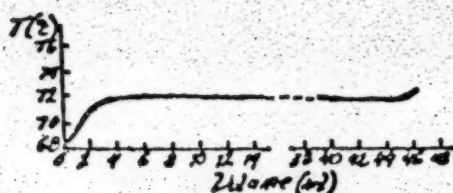1) pressure 31 mm; 2) pressure 39 mm.

Fig. 2. Fractionation curve for 2-methyl-1,5-hexadien-3-one; pressure 42 mm.

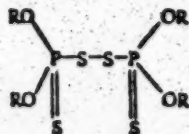• See Consultants Bureau translation, page a 331 ff.

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ORGANOPHOSPHORUS COMPOUNDS:
O,O-DIALKYL HYDROGEN PHOSPHOROTHIOLOTHIONATES

M. I. Kabachnik and T. A. Mastryukova

In an investigation of the reaction of tetraphosphorus heptasulfide P_4S_7 with alcohols, we found [1] that one of the products was an O,O-dialkyl hydrogen phosphorothiolothionate $(RO)_2PSSH$, which we obtained as a colorless liquid that could be distilled under reduced pressure. This group of substances has already been known for about a century. They were first obtained in 1859 by Carius [2] by the reaction of alcohols with phosphorus "pentasulfide", but Carius proposed an incorrect equation for this reaction. Later, Pishchimuka [3] verified the work of Carius and found that practically the only organophosphorus compounds formed in this reaction are the O,O-dialkyl hydrogen phosphorothiolothionates; Pishchimuka also gave the correct equation for this reaction [4]. In 1945 Mann and coworkers [5] confirmed that the structure of these phosphorothiolothionates was in accord with the formula $(RO)_2PSSH$. Finally, O,O-dialkyl hydrogen phosphorothiolothionates and their salts have been described in numerous patents.

All the workers who have previously prepared O,O-dialkyl hydrogen phosphorothiolothionates have described them as undistillable slurps, have not analyzed them, and have characterized them only in the form of their salts. Our preparation of these phosphorothiolothionates in the form of colorless liquids that could be vacuum-distilled caused us to doubt the identity of the dialkyl hydrogen phosphorodithioates obtained from the phosphorus sulfides P_4S_7 and P_4S_{10}. We repeated the reaction of the decasulfide P_4S_{10} with alcohols and found, in complete agreement with the results of Pishchimuka, that the main products were O,O-dialkyl hydrogen phosphorothiolothionates. Again, however, colorless liquids that could be vacuum-distilled were obtained, and their description on many occasions as undistillable slurps must be considered to be a misunderstanding. We, therefore, have obtained these substances in the pure form for the first time. We give a table showing the properties of O,O-dialkyl hydrogen phosphorothiolothionates obtained from the phosphorus sulfides P_4S_7 and P_4S_{10} (Table 1).

TABLE 1

Formula	Prepared from	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	Yield (%)
$(CH_3O)_2PSSH$	P_4S_{10}	62-63	4.5	1.2888	1.5333	73.2
$(C_2H_5O)_2PSSH$	P_4S_{10}	81-82	5	1.1654	1.5076	76.5
$(C_2H_5O)_2PSSH$	P_4S_7	97-98	12	1.1650	1.5105	15.4
$(n-C_3H_7O)_2PSSH$	P_4S_{10}	81.5-82.5	2	—	1.4986	75.0
$(n-C_3H_7O)_2PSSH$	P_4S_7	85-86	3	1.1040	1.4987	6.5
$(i-C_3H_7O)_2PSSH$	P_4S_{10}	71-72	3	1.0911	1.4918	60.0
$(i-C_3H_7O)_2PSSH$	P_4S_7	70.5-71.5	3	1.0913	1.4920	25.4

There is complete agreement between the constants of the O,O-dialkyl hydrogen phosphorothiolothionates obtained from the two sulfides P_4S_7 and P_4S_{10}. The dibutyl compound was the only one of the esters that was not successfully vacuum-distilled, and this was therefore isolated as its mercury salt, m.p. 60-61°. The melting points of the mercury salts prepared from the sulfides P_4S_7 and P_4S_{10} were identical, and a mixed test showed no depression. In the same way the corresponding single and mixed melting points were identical for salts prepared from the distillable phosphorothiolothionates obtained from P_4S_7 and P_4S_{10} (Table 2).

O,O-Dialkyl hydrogen phosphorothiolothionates are colorless highly refractive liquids, smelling of hydrogen sulfide; they are soluble in organic solvents and in alkalis, and the lower members are soluble in water. They may be titrated as strong monobasic acids in aqueous and alcoholic medium. O,O-Dialkyl hydrogen phosphorothiolothionates are readily oxidized in an alkaline solution of iodine with formation of the corresponding disulfides:

We prepared disulfides having R = CH_3, C_2H_5, and $i-C_3H_7$. They are water-insoluble crystalline substances.

Formula	M.p. (°C)		Data in the literature
	this work		
	from P_4S_7	from P_4S_{11}	
[(CH$_3$O)$_2$PSS]$_2$Ni	—	124-125	123° [6]
[(C$_2$H$_5$O)$_2$PSS]$_2$Pb	75-76	75-76	74° [3,5]
[(i-C$_3$H$_7$O)$_2$PSS]$_2$Pb	130-131	130-131	—
[(n-C$_4$H$_9$O)$_2$PSS]$_2$Hg	60-61	60-61	61-62° [5]

Formula	Equivalent	
	Found	Calc.
(CH$_3$O)$_2$PSSH	161.3; 161.2	158
(C$_2$H$_5$O)$_2$PSSH	183.8; 189.0	186
(n-C$_3$H$_7$O)$_2$PSSH	216.6; 216.7	214
(i-C$_3$H$_7$O)$_2$PSSH	216.7; 217.5	214

EXPERIMENTAL

Reaction of the Decasulfide P_4S_{11} with Alcohols

The anhyrous alcohol was introduced into a round-bottomed flask having a two-way adapter connected to a reflux condenser protected with a calcium chloride tube, and the phosphorus sulfide was added in small portions. The lower alcohols reacted vigorously, but heating was required for the reaction of butyl alcohol with the decasulfide P_4S_{11}. The mixture was heated in a water bath until evolution of hydrogen sulfide ceased (for butyl alcohol this required 7-8 hours' heating). The reaction mixture was then filtered, if necessary, and fractionated, first at atmospheric pressure and at 30-40 mm to remove the alcohol, after which the reaction product was vacuum-distilled.

O,O-Dimethyl Hydrogen Phosphorothiolothionate. The substances taken were P_4S_{11} (33.3 g) and methyl alcohol (24.0 g). The whole of the phosphorus sulfide reacted, practically without residue. The fractions obtained at 4.5 mm were:

Fraction I, b.p. 41-62°: 3.5 g
Fraction II, b.p. 62-63°: 34.7 g (yield 73%)
Fraction III, b.p. 63-71°: 5.1 g

For Fraction II: n_D^{18} 1.5343; d_4^{18} 1.2888; σ_{18} 38.87; found MR_D 38.13; calculated MR_D 38.34.

Found %: P 19.51, 19.60; Parachor 306.1
$C_2H_7O_2PS_2$. Calculated %: P 19.62; Parachor 303.0

Nickel Bis(O,O-dimethyl Phosphorothiolothionate) [(CH$_3$O)$_2$PSS]$_2$Ni. Nickel chloride (1.29 g) was added to a neutralized solution of O,O-dimethyl hydrogen phosphorothiolothionate (3.16 g), and the dark colored solution was evaporated to dryness. The nickel salt was separated from sodium chloride by recrystallization from benzene, and 3.5 g of nickel bis(O,O-dimethyl phosphorothiolothionate) was obtained in the form of glistening leaves of a bright lilac color, m.p. 124-125° (literature gives 123° [6]).

O,O-Diethyl Hydrogen Phosphorothiolothionate. The substances taken were P_4S_{11} (50.8 g) and ethyl alcohol (69.0 g). The solid residue after the reaction weighed 3.2 g, and 65.1 g (76.5%) was obtained of a substance of b.p. 81.5-82.5°/5 mm; n_D^{18} 1.5076; d_4^{18} 1.1654; σ_{18} 31.7; found MR_D 47.54; calculated MR_D 47.58.

Found: Parachor 378.7
$C_4H_{11}O_2PS_2$. Calculated: Parachor 379.8

The constants of the same substance, obtained from P_4S_7 [1], had b.p. 97-98° at 12 mm; n_D^{18} 1.5105; d_4^{18} 1.1650; σ_{18} 31.7.

Lead Bis(O,O-diethylPhosphorothiolothionate) [(C$_2$H$_5$O)$_2$PSS]$_2$Pb. This was prepared as previously described [1]. M.p. 75-76° (from alcohol). Mixed test with lead salt obtained from P_4S_7 [1] and according to Malatesta [5] gave the result: 75-76°.

O,O-Dipropyl Hydrogen Phosphorothiolothionate. The substances taken were P_4S_{11} (11.1 g) and propyl alcohol (12 g). There was no residue, and 16.1 g (75.0%) was obtained of a substance of b.p. 81.5-82.5°/2 mm and n_D^{18} 1.4986. The constants of the thio ester (n-C$_3$H$_7$O)$_2$PSSH obtained from P_4S_7 were b.p. 85-86°/3 mm and n_D^{18} 1.4987.

O,O-Diisopropyl Hydrogen Phosphorothioloth'onate. This was prepared from 5.6 g of P_4S_{11} and 6 g of isopropyl alcohol. There was no residue, and 6.4 g (60%) of the diisopropyl hydrogen phosphorothiolothionate, b.p. 71-72° at 3 mm and n_D^{18} 1.4918, was obtained. The constants of the thio ester (i-$C_3H_7O)_2$PSSH obtained from P_4S_7 were b.p. 70.5-71.5° at 3 mm, n_D^{18} 1.4920 [1].

Lead Bis(O,O-diisopropyl Phosphorothiolothionate) [(i-$C_3H_7O)_2$PSS]$_2$Pb. O,O-Diisopropyl hydrogen phosphorothiolothionate (4.28 g) was neutralized with caustic soda (phenolphthalein), and the solution was mixed with lead acetate (3.79 g). White curds (7.4 g) were obtained. Two crystallizations from alcohol yielded 5.1 g of the lead salt in the form of fine silky snow-white needles, m.p. 130-131°. The melting point of the lead salt obtained in the same way from P_4S_7 [1] was 130-131°, and a mixed test gave no depression.

$$\text{Found \%: S 24.95; 25.17}$$
$C_{12}H_{28}O_4P_2S_4$Pb. Calculated %: S25.00

Mercury Bis(O,O-dibutyl Phosphorothiolothionate). The substances taken were P_4S_{11} (11.1 g) and butyl alcohol (14.8 g); there was no residue. The dark-colored reaction mixture was neutralized with 10% caustic soda, the small amount of oil that separated as a layer was removed, and the aqueous layer was washed with ether. Mercuric chloride (12 g) was then added, and the mercury salt was precipitated from the aqueous solution in the form of an oil. It was extracted with ether, and the ether extract was dried over calcium chloride. After evaporation of the ether, 25 g of salt, m.p. 56-68°, was obtained. The melting point after recrystallization from methyl alcohol was 60-61°. The melting points of the same salt prepared from P_4S_7 [1] and according to Mastin [5] were 60-61° and 61-62° respectively. Mixed tests showed no depression (60-60.5°).

Titration of O,O-Dialkyl Hydrogen Phosphorothiolothionates

All of the phosphorothiolothionates were readily soluble in a sufficiently large amount of titration alkali, the excess of which could be exactly back-titrated. The following titration results were obtained (Table 3).

Oxidation of the O,O-Dialkyl Hydrogen Phosphorothiolothionates with Iodine

The disulfide
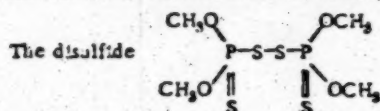
was obtained as follows: O,O-dimethyl hydrogen phosphoro-thiolothionate (4.8 g) was dissolved in an equivalent amount of aqueous caustic soda. A solution of iodine (3.8 g) in aqueous potassium iodide was added. The yellowish precipitate that formed was filtered off and dried (4.5 g, m.p. 48-49.5°), and was then recrystallized from hexane, yielding 3.5 g (74.3%) of the disulfide, m.p. 51-52°, a substance that is soluble in organic solvents, but insoluble in water.

$$\text{Found \%: C 15.50; 15.32; H 3.61; 3.56; P 19.57; 19.59; S 40.20; 40.26}$$
$C_4H_{12}O_4P_2S_4$. Calculated %: C 15.29; H 3.82; P 19.74; S 40.76

The disulfide
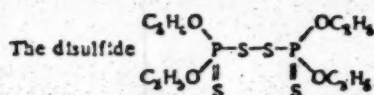
was prepared similarly to the previous one from 9.3 g of O,O-diethyl hydrogen phosphorothiolothionate and 6.39 g of iodine. It came down as an oil and was extracted with ether; the ether solution was dried over sodium sulfate, and the ether was evaporated off. The residue crystallized out when cooled with dry ice. The crystals were filtered off and washed well with hexane. The product, 4.3 g (48%) of cubic crystals, was readily soluble in organic solvents and insoluble in water.

$$\text{Found \%: P 16.84; 16.89}$$
$C_8H_{20}O_4P_2S_4$. Calculated %: P 16.76

The disulfide
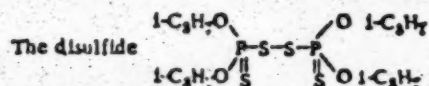
was prepared similarly to the previous one from 8.5 g of O,O-diisopropyl hydrogen phosphorothiolothionate and 5 g of iodine in neutral aqueous solution. It came down as a colorless curdy finely crystalline precipitate. The yield of crude product was 8.3 g (97.4%); yield after recrystallization from ethyl alcohol 7.05 g (82.75%), m.p. 91-92°, not changing after a second crystallization. Soluble in organic solvents.

Found %: C 33.84; 33.74; H 6.53; 6.56; P 14.54; 14.40; S 29.58; 29.84

$C_{12}H_{28}O_4P_2S_4$ Calculated %: C 33.80; H 6.57; P 14.55; S 30.05

Found M: 417; 434.9 (cryoscopically in benzene)

Calculated M: 426

SUMMARY

1. For the first time O,O-dialkyl hydrogen phosphorothiolothionates have been prepared in the pure state in the form of liquids that may be vacuum-distilled. Some of their properties have been investigated.

2. It has been shown that the dialkyl hydrogen phosphorodithioates formed by the reaction of alcohols with the two phosphorus sulfides P_4S_7 and P_4S_{10} are identical.

3. It has been shown that, when O,O-dialkyl hydrogen phosphorothiolothionates are oxidized with iodine, the corresponding disulfides are formed.

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* See Consultants Bureau English translation, page 661 ff.

CRYSTALLINE ORGANOLITHIUM COMPOUNDS.
COMPOUNDS OF THE AROMATIC SERIES

T. V. Talalaeva and K. A. Kocheshkov

Although aromatic organolithium compounds have been frequently described in solution (mainly ethereal and containing also appreciable amounts of lithium halides, diaryls, finely divided lithium, etc.), there is only one example in the literature of the isolation of a crystalline aromatic organolithium compound [1], namely phenyllithium:

$$(C_6H_5)_2Hg + 2C_2H_5Li \longrightarrow (C_6H_5)_2Hg + 2C_6H_5Li \tag{1}$$
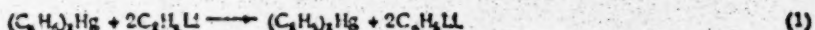
Improved and more general methods of preparing pure crystalline compounds are, however, of considerable interest. For carrying out a number of precise, for example physicochemical, investigations relating to complex formation, we required pure crystalline compounds, or pure solutions prepared from these.

The method indicated in Equation 1 suffered from two inherent defects: 1) in the metathetic reaction diethylmercury is formed, and its high toxicity is well known; 2) the preparation of pure ethyllithium is based on the reaction between diethylmercury and lithium. As we had successfully solved the problem of preparing pure crystalline ethyllithium [2], it was necessary to solve also the problem of the replacement in these metathetic reactions of organomercury compounds by other organometallic (or "organoelemental") compounds.

The previously described [3] metathetic reactions between organoelemental compounds and alkyllithiums were not carried out with the object of isolating crystalline organolithium compounds (the presence of these was proved by the formation of carboxylic acids by carbonation of their solutions, the authors' problem being the investigation of the relative strengths of the bonds between the radicals and the various elements. However, as we have shown [2], these metathetic reactions can be widely and successfully applied for the preparation of crystalline organolithium compounds. In this respect different organoelemental compounds are not all of equal value. thus the reactions of RLi with aromatic bromo compounds have the important defect that the secondary condensation reaction II generally occurs:

$$ArBr + RLi \longrightarrow ArLi + RBr; \tag{I}$$
$$ArLi + RBr \longrightarrow ArR + LiBr \tag{II}$$

leading to formation of lithium halide, whose solubility in organic solvents is close to that of the aryllithium formed.

In our monograph [4], and also in a paper published in 1951 [2], we emphasized both the undesirability of heating, which accelerates the condensation reaction, and also the necessity for testing for the presence of halide ions in the preparations of aryllithium compounds obtained by this method. Mikhailov and Chemova [5] in their more recent investigations, while applying our methods for the isolation of aryllithium compounds in the bromoarene portion, made no reference to our work and also, unfortunately, did not follow our advice concerning the above-mentioned defects of this reaction.

By applying heating (or by permitting "rapid spontaneous temperature rise" in the preparation of complexes), they created conditions favorable for the condensation reaction and the formation of lithium bromide. Moreover, in the description of the compounds (which they evidently did not isolate, but either used for reaction or decomposed for analysis, directly in the filtration apparatus) there are no indications even of a qualitative test for halide ion. This remark relates particularly to the direct reaction between bromobenzene and lithium. The presence of lithium halide impurity, however, could have greatly affected their results relating to aryllithiums and their etherates (or other complexes), since the possibility of the formation of more complicated compounds was now present.

For example, the well formed crystals that separate from concentrated ethereal solutions of phenyllithium (prepared from bromobenzene and lithium), if analyzed only for lithium (titration with acid), might

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be taken for the monoetherate or dietherate of phenyllithium. Actually, ternary complexes containing LiBr [6] come down*, and their lithium contents (by titration with acid) happen to be near to those required by the formulas $C_6H_5Li \cdot (C_2H_5)_2O$ and $C_6H_5Li \cdot 2(C_2H_5)_2O$. Mikhailov and Chernova [7] by omitting to detect the presence of lithium bromide in the analysis, came to an incorrect conclusion concerning the formula of their etherate. Incidentally, the authors pass over in silence the fact that the complex nature of uncolored organo-lithium compounds was first pointed out by us [6].

With regard to the complex nature of colored organolithium compounds, in spite of Mikhailov and Chernova's assertion [7] that the study of the colored and electrically conducting organic compounds of the alkali metals had led them to the "discovery" of the complex nature of substances of this type, we may remark that this fact was already known 25 years ago. In 1926 the complex of triphenylmethyllithium with two molecules of ether (giving good analysis) was isolated [8]; the amine $(C_6H_5)_3CNa \cdot NH_3$ is also known [9]. We cannot believe that Mikhailov and Chernova were not acquainted with the basic original literature on organolithium compounds, but in describing [5] the long known synthesis of the dietherate of triphenylmethyl-lithium they made no reference to the original source.

We considered that a more expedient route to pure crystalline aryllithium compounds (not containing unavoidable halide impurities) was by the well known metathetic "metal-metal" reaction [3,4]. As compounds of lead (owing to their toxicity) or tin (owing to the sluggishness of the reaction) were inconvenient, we decided to use organoantimony compounds.

For antimony (and correspondingly for bismuth) the reaction is expressed by the following equation:

$$Ar_3Sb + 3C_2H_5Li \longrightarrow 3ArLi + (C_2H_5)_3Sb$$
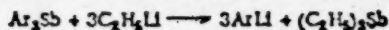
and the isolation of ArLi is based on the fact that the original aromatic compound Ar_3Sb (or Ar_3Bi) is soluble in benzene and the ethyllithium that reacts with it is also soluble in benzene, whereas of the two products obtained only the aryllithium is precipitated from solution so that it can be isolated in a pure state. The reaction goes under mild conditions (temperature not above 30-40°), relatively slowly, and with a characteristic, often long, induction period.

By this method the following crystalline organolithium compounds of the aromatic series were prepared (from organoantimony compounds): p-tolyllithium (yield 72-82%), o-tolyllithium (62%), m-tolyllithium (48%), phenyllithium (80%), p-bromophenyllithium (quantitative), p-chlorophenyllithium (45.8%), 1-naphthyllithium (46.4%). It is interesting to note that it was not found possible to isolate any phenyllithium when triphenyl-bismuth was used.

The metathetic reaction with haloarenes (iodo- and bromo-):

$$ArX + C_2H_5Li \longrightarrow ArLi + C_2H_5X$$

is much more rapid (from several seconds to several hours, depending on the radical), even at room temperature. The reaction, unlike those with Ar_3Sb, begins immediately. In all cases analysis was made not only for lithium content, but also for the presence of halide ions. It should be noted that the organolithium compounds obtained always contained some lithium halide impurity, and the amount of this could be fairly considerable when heat was used or the reaction was prolonged.

By this reaction the following compounds were obtained from iodo compounds: o-tolyllithium (53.6%), m-tolyllithium (30%), phenyllithium (52.1%). The following were obtained from bromo compounds: p-tolyllithium (66.0%), phenyllithium (78%), p-bromophenyllithium (76.1%), p-chlorophenyllithium (88.8%), 4-biphenyllithium (44.4%). The crystalline aromatic organolithium compounds obtained were infusible substances (tests were made in a capillary filled with nitrogen), readily soluble in absolute ether, and insoluble in benzene, hexane, and petroleum ether. In the air p-bromophenyllithium and o-tolyllithium ignited (yellow flame); phenyllithium charred and smoldered. All the compounds reacted with water with a flash and charring.

Large crystals of p-chlorophenyllithium and 1-naphthyllithium became white on the surface when decomposing in the air, but they continued to give the qualitative reaction for ArLi with Michler's ketone. The compounds

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* They are similar, to a certain extent, to the organomagnesium complexes, e.g. $2ArLi \cdot LiBr \cdot 2(C_2H_5)_2O$.

obtained gave the usual reactions of organolithium compounds (see, for example the reaction of phenyllithium with benzophenone and with stannic chloride, also the color reactions).

EXPERIMENTAL

Owing to the sensitivity of organolithium compounds to the moisture, carbon dioxide, and oxygen in the air, the work with them was carried out in an atmosphere of pure dry nitrogen. We used nitrogen from cylinders (oxygen content not higher than 0.3%), and purified it by passing it through two furnaces, each 1 meter long, containing copper turnings at 450°, and three columns of the same length containing solid caustic potash, calcium chloride, and phosphoric oxide on glass wool respectively.

The reactions were carried out in apparatus with standard joints (Figures 1 and 2). The upper openings of the vessels (narrow joint A) served for the addition of the solutions and the stirring of the precipitate; also, when necessary, a reflux condenser was attached at this joint. The side tubes of the vessels (wider joint B) served for the connection of the filtration apparatus (Figure 3), and also, sometimes, of a dropping funnel. The joints were lubricated with silicone grease. Before use, the apparatus was carefully dried at 120° and cooled while a current of nitrogen was passing. The three-way tap at the side of the apparatus (C, Figures 1 and 2) permitted connection to the stream of nitrogen, which terminated in a drying system consisting of V-shaped tubes containing phosphoric oxide on glass wool, calcium chloride, and sulfuric acid. The last tube served for the control of the rate at which the nitrogen left. If necessary, 6-8 pieces of apparatus could be connected in series through the tap C. They were connected by means of thick-walled, elastic, red rubber tubing. Such a connection system permitted the apparatus to be maintained under a small pressure of nitrogen, even when the caps at A and B (Figures 1 and 2) were removed for a short time (the reaction mixture was always protected by a stream of nitrogen).
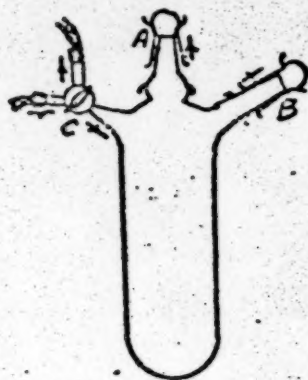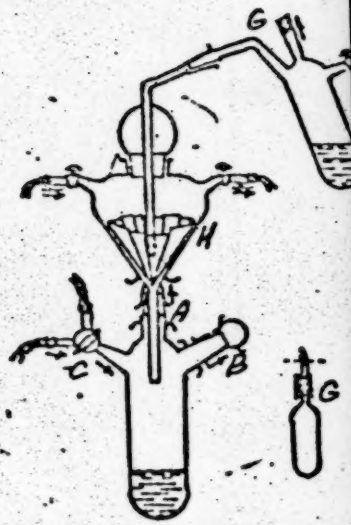

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

The apparatus represented in Fig. 3 was used for filtration. When the substance had been completely transferred to the filter, the first apparatus was disconnected and the upper opening of the filtration apparatus was closed with a stopper. The residue on the filter was washed three or four times with pentane and the receiver for the filtrate E was disconnected, the lower end of the apparatus being connected to the drying system (see above). The apparatus was turned on its side (side tube upwards), and the precipitate was distributed over the whole length of the apparatus by tapping. The precipitate was dried in the nitrogen stream until it could be readily poured out. It is not recommended that the precipitate be dried on the filter by passing nitrogen through it. The dry substance was sealed in tubes, which were connected to the side tube. The tubes were previously filled with nitrogen (otherwise charring and decomposition might occur).

The dissolution of ethyllithium in benzene was carried out in the vessel F (Fig. 4). Very often, particularly when large amounts (3-4 g) of ethyllithium were taken, turbid solutions were obtained; they were filtered in the apparatus H through an ordinary folded filter paper previously dried over phosphoric oxide. The direction of the nitrogen stream is indicated by arrows in all the diagrams. Vessels of various dimensions were taken; the reaction vessels (Figures 1 and 2) had volumes from 15 to 500 ml, and the volume of the filtration apparatus varied correspondingly (Figures 3 and 4). All the solvents must be pure and dry (thiophene-free benzene).

Preparation of p-Tolyllithium

a) From Tri-p-tolylantimony [11]. In an apparatus provided with a magnetic stirrer (Fig. 2) 82 ml of a solution of ethyllithium (1.61 g, i.e. 0.042 m.ole) in benzene was placed, and 10 ml of a hot (35-40°) benzene solution of tri-p-tolylantimony (3.9 g, i.e. 0.01 mole) was added. There was no noticeable reaction. The mixture was stirred for six hours at 18-20°, and then for 14 hours at 30-35°. At the end of this period a sharp increase in the turbidity of the solution was to be observed, and after 5-10 minutes the solution became quite opaque owing to the presence of a fine white precipitate of p-tolyllithium. Stirring was continued at 30-35° for a further 40 hours. The filtration apparatus (Fig. 3) was then attached in a stream of nitrogen to the side tube; nitrogen was passed for five minutes, and filtration was then effected under a pressure of nitrogen. The very fine white precipitate was very readily transferred to the filter; it was washed on the filter with pentane (four portions of 15 ml), dried in a stream of nitrogen at 35-40° for one hour, and sealed in tubes. The yield was 72-80%, calculated on the tri-p-tolylantimony taken. The reaction may be carried out in the apparatus shown in Fig. 1, without stirring. The yield is of the same order, but larger crystals are obtained.

Found %: Li 7.26; 7.28

C₇H₇Li Calculated %: Li 7.08

When p-tolyllithium crystals are poured out in the air, they do not ignite spontaneously; on coming into contact with water or alcohol, they decompose with a strong hissing noise accompanied by charring and sometimes by a yellow burst of flame. P-Tolyllithium is infusible, and is readily soluble in ether, but poorly soluble in benzene and hexane; it gives the usual color reaction with Michler's ketone. When this test is done with p-tolyllithium in benzene solution, it is necessary to heat the mixture to the boil (owing to the poor solubility of the lithium compound in benzene).

b) From Tri-p-tolylbismuth. In the apparatus shown in Fig. 1, 15 ml of a benzene solution of ethyllithium (0.69 g, i.e. 0.019 mole) was placed, and a solution of 2.4 g (0.005 mole) of tri-p-tolylbismuth [12] in 5 ml of benzene was added. When the solutions were mixed, a very slight yellowing was observed. The reaction mixture was set aside at room temperature, and after about a month the formation of isolated large clear crystals was to be observed on the sides of the vessel; the quantity of these gradually increased. They were then filtered off from the solution, washed twice with pentane (10 ml each time), dried, and sealed in tubes. The yellowish crystals obtained weighed 0.965 g (66.1%).

Found %: Li 7.09; 7.03

C₇H₇Li Calculated %: Li 7.08

c) From p-Bromotoluene. p-Bromotoluene (1.7 g, i.e. 0.01 mole) dissolved in 5 ml of benzene was added to 0.56 g (0.01 mole) of ethyllithium in 15 ml of benzene. No changes occurred when the solutions were mixed. After one day, characteristic large crystals of p-tolyllithium, together with a small amount of fine precipitate, separated. The usual treatment yielded 0.64 g (66 %) of p-tolyllithium containing some lithium bromide as impurity.

Found %: Li 6.31; 6.32

C₇H₇Li Calculated %: Li 7.08

Preparation of o-Tolyllithium

a) **From Tri-o-tolylantimony.** From 15 ml of a benzene solution of ethyllithium (0.69 g. i.e. 0.010 mole) and 1.97 g (0.005 mole) of tri-o-tolylantimony in 10 ml of benzene, treated under the usual conditions (see above), a fine precipitate of o-tolyllithium (0.9 g, 62%) was obtained after the mixture had been allowed to stand at room temperature for two weeks.

Found %: Li 6.95; 6.87
C_7H_7Li Calculated %: Li 7.08

b) **From o-iodotoluene.** From 0.36 g (0.01 mole) of ethyllithium in 16 ml of benzene and 2.17 g (0.01 mole) of o-iodotoluene in 10 ml of benzene, a very fine voluminous white precipitate was obtained (after mixing there was a slight rise in temperature). After standing for 30 minutes, the precipitate was filtered off (it filtered very slowly), and was washed as usual with pentane and dried.. A positive test for halide was obtained. The yield of o-tolyllithium was 0.62 g (53.0%).

Found %: Li 7.37; 7.12
C_7H_7Li Calculated %: Li 7.08

Preparation of m-Tolyllithium

a) **From Tri-m-tolylantimony.** A benzene solution (15 ml) containing 0.69 g (0.010 mole) of ethyllithium and 1.97 g (0.005 mole) of tri-m-tolylantimony in 15 ml of benzene were taken. The solution was set aside for two weeks at room temperature and after the usual treatment it yielded 0.7 g (48%) of m-tolyllithium in the form of a finely crystalline white precipitate.

Found %: Li 6.92; 6.81
C_7H_7Li Calculated %: Li 7.08

b) **From m-iodotoluene.** The substances taken were ethyllithium (0.36 g, i.e. 0.01 mole) in 17 ml benzene and m-iodotoluene (2.17 g, i.e. 0.01 mole) in 10 ml of benzene. Mixing was accompanied by slight turbidity, and the mixture, after standing for two days, yielded 0.29 g (30%) of m-tolyllithium in the form of a fine yellowish powder. In the air the substance darkened and smoldered.; It reacted with alcohol with a burst of yellow flame. A positive test for halide was obtained.

Found %: Li 6.73; 6.70
C_7H_7Li Calculated %: Li 7.08

Preparation of Phenyllithium

a) **From Triphenylantimony.** Triphenylantimony (2.25 g, i.e. 0.006 mole) in 15 ml of benzene was added to ethyllithium (0.75 g, i.e. 0.021 mole) in 15 ml of benzene. After a three-hour heating at a gentle boil (the liquid yellowed slightly), the separation of white needles suddenly began. The amount of these quickly increased, and after 10-15 minutes they filled the whole of the solution. Heating was continued for two hours, and was followed by cooling to room temperature, filtration, four washes with pentane and drying. The yield was 0.8 g (50%).

In another experiment (0.3 g of ethyllithium, 5 g of triphenylantimony, in 50 ml of benzene, under the same conditions) separation of crystals was observed already after 30 minutes. The yield of phenyllithium was 2.23 g (41%).

Found %: Li 8.28; 8.09
C_6H_5Li Calculated %: Li 8.27

Phenyllithium forms infusible white needles. On coming into contact with air. It smolders, without igniting (the spontaneous inflammability of phenyllithium, described in the literature, must be ascribed to the presence of ethyllithium as impurity). When put into water, phenyllithium decomposes with much hissing and bursts of flame (yellowish). It is of poor solubility in benzene and petroleum ether, and readily soluble in absolute ether.

b) **From Iodobenzene.** When solutions, previously cooled to + 5° of 0.36 g (0.01 mole) of ethyllithium in 17 ml of benzene and of 2 g (0.01 mole) of iodobenzene in 10 ml of benzene were mixed, there was a slight evolution of heat and the whole mass solidified (the behavior is similar to that which we have observed when a benzene solution of butyllithium acts upon diphenylmercury). A small amount of isopentane was added, and the precipitate was rubbed out with a rod and filtered off. It was washed three times with pentane (15 ml each time), and dried at 35-40°. The

yield of phenyllithium, in the form of a fine powder, was 0.44 g (52.1%). A positive test for halide was obtained.

<center>
Found %: Li 7.95; 8.00
C₆H₅Li Calculated %: Li 8.27
</center>

c) From Bromobenzene. When 0.36 g (0.01 mole) of ethyllithium in 15 ml of benzene was mixed with 1.56 g (0.01 mole) of bromobenzene in 5 ml of benzene and the mixture was allowed to stand for two hours, a slight turbidity appeared which gradually increased in intensity. After one day characteristic crystals of phenyllithium had separated. A further day was allowed for completion of the reaction, and the usual treatment followed, giving 0.65 g (78%) of phenyllithium. The substance contained lithium bromide as impurity. It should be noted that when the reaction mixture containing the crystals of phenyllithium was allowed to stand for a longer period (more than a month), a gradual disappearance of the characteristic crystalline precipitate was observed, and the separation of a small amount of a more compact fine white precipitate of lithium bromide occurred (as a result of the condensation reaction).

<center>
Found %: Li 6.97; 7.03
C₆H₅Li Calculated %: Li 8.27
</center>

Preparation of Tetraphenyltin. Absolute ether (40ml) was introduced under nitrogen into a round-bottomed four-necked flask fitted with dropping funnel, reflux condenser, tube for the passage of nitrogen, and mercury-sealed stirrer. Crystalline phenyllithium (1.57 g) was dissolved in the ether, and with stirring and external ice cooling stannic bromide (2 g) in dry benzene (10 ml) was added. Before the last portion of the stannic bromide solution had been added, a test with Michler's ketone was positive; after the addition it was negative. The mixture was boiled gently with stirring for two hours. The usual treatment yielded 1.58 g (79%) of tetraphenyltin, m.p. 224-225°. In the residue from the separation of (C₆H₅)₄Sn, a test with an alcoholic solution of silver nitrate gave considerable blackening, indicating the presence of hexaphenyldistannane.

Preparation of Triphenylmethanol. The preparation was carried out in the same apparatus. Absolute ether (25 ml) was poured in, and then a tube of crystalline phenyllithium (0.35 g, i.e. 1 mole) was opened and its contents were sprinkled in through the side tube of the flask in a counter current of nitrogen. The crystals dissolved immediately. Benzophenone (0.76 g, i.e. 1 mole) was dissolved in absolute ether (20 ml), and the solution was added, the course of the reaction being checked by qualitative tests with Michler's ketone for the presence of phenyllithium. The amount added before the test became negative was 18 ml, i.e. 0.72 g of benzophenone. The reaction mixture was stirred further for an hour at room temperature, and the usual treatment then yielded 0.65 g of slightly greyish crystals (70% calculated on the amount of benzophenone taken for reaction). The melting point after recrystallization from alcohol was 162°.

Preparation of p-Bromophenyllithium

a) From Tri-p-bromophenylantimony. A warm solution of 2.9 g (0.005 mole) of tri-p-bromophenylantimony in 15 ml of benzene (it was necessary to warm for complete solution) was added under nitrogen to 30 ml of a benzene solution of ethyllithium (0.79 g, i.e. 0.022 mole). Some yellowing and clouding was observed when the solutions were mixed. The solution was allowed to stand at room temperature. After 30 minutes the turbidity had appreciably increased, and after an hour the solution was completely opaque and was full of a white suspension that gradually settled. After 12 hours from the start of the reaction, the reaction vessel was about two-thirds full of white precipitate, above which was a clear, almost colorless solution. The precipitate was filtered off, washed with two 15 ml portions of pentane, and dried in a current of nitrogen at 40-45° for one hour. The very fine white powder obtained was sealed in tubes. The yield was quantitative.

<center>
Found %: Li 4.15; 4.16
BrC₆H₄Li Calculated %: Li 4.28
</center>

In the air, p-bromophenyllithium immediately ignites with a yellow flame. The bursts of flame are similar (intensity) to those given by ethyllithium. A few crystals introduced under nitrogen into a benzene solution of Michler's ketone and treated in the usual way give an intense green coloration.

b) From p-Dibromobenzene. The solutions taken were: 0.18 g (0.005 mole) of ethyllithium in 10 ml of benzene, and 1.17 g (0.005 mole) of p-dibromobenzene in 5 ml of benzene. As soon as the solutions were mixed, a strong turbidity appeared, and after one hour a considerable amount of precipitate had separated. The mixture was allowed to stand for six hours, and after the usual treatment 0.61 g (76.1%) of p-bromophenyllithium was isolated. A positive test for halide was obtained.

<center>
Found %: Li 4.91; 4.65
BrC₆H₄Li Calculated %: Li 4.28
</center>

Preparation of p-Chlorophenyllithium.

a) From tri-p-chlorophenylantimony. A solution of 2.28 g (0.005 mole) of tri-p-chlorophenylantimony in 10 ml of benzene was added to 30 ml of a solution of ethyllithium (0.79 g, i.e. 0.022 mole); slight yellowing occurred. The solution was allowed to stand at 18-20°. After about one hour some fine white crystals had appeared on the bottom of the vessel, and after three days the amount of crystals had reached its maximum. The solution was then filtered under nitrogen and the precipitate was washed with benzene and pentane and dried in a current of nitrogen for 30 minutes at 35-45°, yielding 0.8 g (45.8%) of p-chlorophenyllithium.

Found %: Li 5.64; 5.82

ClC_6H_4Li Calculated %: Li 5.86

The substance does not burn in the air, but slowly turns white. A crystal that has lain in the air for about two minutes and has become white at the surface will still give an intensive green coloration when heated with a benzene solution of Michler's ketone and given the usual treatment.

b) From p-bromochlorobenzene. The solutions taken were 0.36 g (0.01 mole) of ethyllithium in 17 ml of benzene and 1.91 g (0.01 mole) of p-bromochlorobenzene in 5 ml of benzene. No changes occurred when the solutions were mixed. After one day large yellowish crystals (1.05 g, 88.6%) of p-chlorophenyllithium separated.

Found %: Li 5.69; 5.62

ClC_6H_4Li Calculated %: Li 5.86

Preparation of 1-Naphthyllithium from Tri-1-naphthylantimony

A suspension of 3.9 g (0.01 mole) of tri-1-naphthylantimony [13] in 15 ml of hot benzene was added to 75 ml of a benzene solution of 1.47 g (0.042 mole) of ethyllithium. The mixture was heated in a water bath at 70-75°, and after about five minutes the tri-1-naphthylantimony went completely into solution. The solution became slightly yellow and after one hour of heating a turbidity appeared, which quickly turned in a precipitate (small). Heating was continued further for five hours, and no increase in the amount of precipitate was observed. The reaction mixture was set aside at room temperature for ten days: Fine dark-colored crystals were to be observed on the walls of the vessel. The solution was filtered and the crystals were washed three times with pentane, dried, and sealed in tubes. The yield of 1-naphthyllithium was 2.18 g (56.4%).

Found %: Li 5.26; 5.10

$C_{10}H_7Li$ Calculated %: Li 5.18

1-Naphthyllithium does not burn in the air. It reacts with water with charring and intense hissing (sometimes accompanied by yellow bursts of flame). It is soluble in absolute ether, and it gives an intense coloration in the Michler's ketone test.

Preparation of 4-Biphenylyllithium from 4-Bromobiphenyl

The solutions taken were 0.18 g (0.005 mole) of ethyllithium in 10 ml of pure benzene and 1.16 g (0.005 mole) of 4-bromobiphenyl in 5 ml of benzene. No changes occurred when the solutions were mixed. After standing for two days, the solution was found to be full of large white matte crystals which formed clusters. The crystals were filtered off, washed with two 10 ml portions of pentane, and dried at 30-35°. The product was 0.35 g (44.4%) of 4-biphenylyllithium in the form of a fine white powder. It contained lithium bromide as impurity.

Found %: Li 3.91; 3.96

$C_{12}H_9Li$ Calculated %: Li 4.33

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SYNTHESIS AND PROPERTIES OF ORGANOSILICON ESTERS
OF MONO- AND DI-BASIC ACIDS

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Only four trialkylsilyl esters (acyloxytrialkylsilanes. $R_3SIOOCR'$) are known. They are all acetic acid derivatives. the alcohol residues being trimethylsilyl [1. 2. 3]. triethylsilyl [4]. tripropylsilyl [5]. and triphenylsilyl [6]. They were prepared by the action of acetic anhydride on $R_3SIOC_2H_5$. or of sodium acetate on R_3SICl. Organosilicon esters of dibasic and higher monobasic acids have not been described in the literature.

With the object of studying the properties of organosilicon esters. we have now undertaken the synthesis of five esters of dibasic acids and three esters of higher monobasic acids. For these syntheses we chose the method. which has not been used previously. of direct reaction of the acids with R_3SICl to give esters of the types $R_3SIOOCR'$ and $R_3SIOOC(CH_2)_x COOSIR_3$:

$$R_3SICl + HOOCR' \rightarrow R_3SIOOCR' + HCl :$$
$$2R_3SICl + HOOC(CH_2)_x COOH \rightarrow R_3SIOOC(CH_2)_x COOSIR_3 + 2HCl.$$
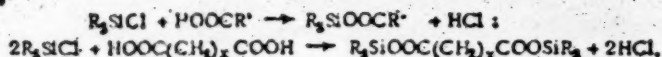
The reaction was carried out by heating a mixture of the components in a flask fitted with reflux condenser and protected by a P_2O_5 column from the action of atmospheric moisture.

All the esters obtained were clear colorless mobile liquids having a feeble characteristic odor. somewhat reminiscent of mold. In their tendency to undergo hydrolysis. the synthesized esters differed notably from their analogs. the organic esters: They were all readily hydrolyzed by dilute solutions of sodium and potassium carbonates. The hydrolysis of certain organosilicon esters of dibasic acids occurred rapidly. even under the influence of atmospheric moisture. as wa readily revealed by the formation of a precipitate of the solid acid. Owing to this. it was not found possible in certain cases to determine the specific gravity of the ester.

Of the five esters of dibasic acids that were synthesized. the trimethylsilyl ester of azelaic acid and the triethylsilyl ester of succinic acid were hydrolyzed exceptionally readily. being almost completely decomposed in the air in the course of 60-90 minutes. The trimethylsilyl ester of adipic acid was somewhat more stable. appreciable hydrolysis being observed only after 15-18 hours. The most stable were the triethylsilyl esters of adipic and azelaic acids. Incipient hydrolysis of the latter was to be observed only after 24 hours. and appreciable hydrolysis of the first ester was to be observed only after 1.5-2 days. even when an addition of water was made.

It would be premature on the basis of these few observations to form any definite conclusions concerning the effect of the molecular weights of the acids and of the hydrocarbon radicals attached to the silicon on the stability to hydrolysis of organosilicon esters. It may be noted only that. in the case of the adipic and azelaic esters studied. the replacement of trimethylsilyl by triethylsilyl increases the stability of the esters to hydrolysis. Owing to the impossibility of using treatments with solutions of sodium or potassium carbonate. the isolation of the esters in the pure state was attained by repeated fractionation at low pressure in a current of dry air. In certain cases elimination of the residual acid was effected by freezing this out in petroleum ether solution. The physiochemical constants of the esters are given in the table.

In absence of an accepted nomenclature for organosilicon esters. the synthesized compounds were named by analogy with the corresponding organic compounds.

EXPERIMENTAL

1. Triethylsilyl Butyrate

a) A mixture of 20 g (0.13 mole) of chlorotriethylsilane and 52 g (0.59 mole) of butyric acid was heated for 85 hours. Two vacuum fractionations yielded 14 g (0.07 mole) of the ester as a colorless mobile liquid. The yield was 52 %.

TABLE

No.	Formula	B.p. (°C)	Pressure (mm Hg)	n_D^{20}	d_4^{20}	MR Found	Calc. *
1	$(C_2H_5)_3SiOOC_3H_7$	85-87	10	1.4250	0.8850	58.46	58.82
		83.5-85 **	9	1.4245	0.8851	58.39	58.82
2	$(C_2H_5)_3SiOOC \cdot CH_2 \cdot CH(CH_3)_2$	92.5-93.5	10	1.4258	—	—	—
3	$(C_2H_5)_3SiOOC \cdot C_6H_{13}$	127.5-129	7	1.4303	—		
4	$[(C_2H_5)_3SiOOC \cdot CH_2]_2$	172.5	10.5	1.4450	0.9518	96.90	96.99
5	$[(CH_3)_3SiOOC \cdot CH_2 \cdot CH_2]_2$	153-154	24.5	1.4275	0.9583	77.84	78.47
6	$[(C_2H_5)_3SiOOC \cdot CH_2 \cdot CH_2]_2$	221-222	26	1.4475	0.9496	105.50	106.25
7	$[(CH_3)_3SiOOC \cdot CH_2 \cdot CH_2 \cdot CH_2]_2CH_2$	180-181	23	1.4310	—	—	—
8	$[(C_2H_5)_3SiOOC \cdot CH_2 \cdot CH_2 \cdot CH_2]_2CH_2$	240-241	22	1.4500	0.9438	118.65	120.14

* MR calculated by E. Warrick's method [8].

** The ester was prepared from sodium butyrate.

Found %: Si 13.89 *; 13.92

$C_{10}H_{22}SiO_2$. Calculated %: Si 13.86

Found ester value **: 263.0; 261.0

$C_{10}H_{22}SiO_2$. Calculated ester value: 277.2

b) A mixture of 37 g (0.25 mole) of chlorotriethylsilane, 93 g (0.75 mole) of dry potassium butyrate, and 300 ml of dry toluene was heated at the boil for 26 hours. The toluene layer was removed from the precipitate by filtration, and the precipitate was washed with a fresh portion of dry toluene, which was then united with the main filtrate. After the toluene had been distilled off, the residue was vacuum-fractionated twice. Two fractions were separated. The yield of ester (the two fractions being treated together for calculation) was 90 %.

Fraction I. b.p. 80-61° / 10 mm; 18 g
Fraction II. b.p. 83.5-85° / 9 mm; 27 g

Analysis of Fraction I:

Found %: Si 12.88; 12.96

Analysis of Fraction II:

Found %: Si 13.57; 13.53

$C_{10}H_{22}SiO_2$. Calculated %: Si 13.86

II. Triethylsilyl Isovalerate

A mixture of 19 g (0.12 mole) of chlorotriethylsilane and 13 g (0.12 mole) of isovaleric acid was heated for 40 hours. Unchanged acid was distilled off, and the residue was treated in the cold with a 10% solution of sodium carbonate and with water, and was dried with anhydrous Na_2SO_4. Two vacuum fractionations yielded a fraction of b.p. 92.5-93.5°/10 mm. The yield was 26 %.

Found %: Si 12.58

$C_{11}H_{24}SiO_2$. Calculated %: Si 12.97

Found ester value: 251.0, 243.0

$C_{11}H_{24}SiO_2$. Calculated ester value: 259.3

III. Triethylsilyl Heptanoate

A mixture of 19 g (0.12 mole) of chlorotriethyl silane and 16 g (0.12 mole) of heptanoic acid was heated for 40 hours. The whole of the reaction product was treated with a solution of sodium carbonate, washed with water, and dried with Na_2SO_4. Fractionation yielded 9 g of triethylsilanol (b.p. 157-158°; n_D^{20} 1.4300). 3 g of

* Silicon was determined by mineralization of a weighed amount by heating with a mixture of concentrated sulfuric and nitric acids.

** The ester value was determined by hydrolysis of a weighed amount with solutions of alkali in diethylene glycol [7].

hexaethyldisiloxane (b.p. 222-233°) and 2 g of a fraction of b.p. 127.5-129°/7 mm.

Analysis of fraction of b.p. 127.5-129°

Found %: Si 9.59; 9.45
$C_{13}H_{34}SiO_2$. Calculated %: Si 11.48
Found ester value: 230.0; 236.0
$C_{13}H_{34}SiO_2$. Calculated ester value: 229.5

IV. Bis(triethylsilyl) Succinate

A mixture of 50 g (0.33 mole) of chlorotriethylsilane and 12 g (0.10 mole) of succinic acid was heated for 107 hours. A semiliquid dark-colored mass formed in the flask. Uncharged acid was removed by filtration through a funnel fitted with a porous plate, and the filtrate was vacuum-fractionated. All the fractions separated contained crystalline acid as impurity. In order to remove this impurity, the main fraction, b.p. 192-195°/18 mm, was washed three times with a 10% solution of sodium carbonate and then with water; it was dried over Na_2SO_4. Repeated fractionation under reduced pressure yielded triethylsilanol (b p. 54°/10.5 mm; n_D^{20} 1.4330; found Si 21.43%; calculated Si 21.10%) succinic acid (b.p. 180°; the literature gives 183°) formed by hydrolysis of the ester, and a small amount of a fraction of b.p. 172.5°/10.5 mm.

Ester value of fraction of b.p. 172.5°:
Found: 309.5; 310.5
$C_{14}H_{34}Si_2O_4$ Calculated: 323.7

V. Bis(trimethylsilyl) Adipate

A mixture of 46 g (0.42 mole) of chlorotrimethylsilane and 25 g (0.17 mole) of adipic acid was heated for 60 hours. Unchanged acid was filtered off with exclusion of moisture, and the filtrate was fractionated in a current of dry air. A fraction was isolated (b.p. 144.5-146°/19 mm) containing a small amount of crystalline acid as impurity. In order to remove this, the fraction was diluted with an equal volume of petroleum ether and cooled to -15°, and the precipitate of acid formed was filtered off at this temperature through a porous glass filter No. 3, with exclusion of moisture. When the petroleum ether was distilled off, it was accompanied by the last traces of solid acid, and 14 g (28%) of ester, b.p. 153-154°/24.5 mm, was obtained.

Found %: Si 17.60; 17.95
$C_{12}H_{26}Si_2O_4$ Calculated %: Si 19.20

The analysis results indicate a low silicon content. This may be explained by the partial evaporation of trimethylsilanol (b.p. 100°) formed by decomposition of the ester during heating with the mixture of H_2SO_4 and HNO_3.

Found ester value: 394.0; 397.0
$C_{12}H_{26}Si_2O_4$ Calculated ester value: 385.6

VI. Bis(triethylsilyl) Adipate

A mixture of 50 g (0.33 mole) of chlorotriethylsilane and 30 g (0.2 mole) of adipic acid was heated for 30 hours. The ester was isolated in the manner described for the preceding experiment. The ester boiled at 221-222°/26 mm.

Found %: Si 14.77
$C_{18}H_{38}Si_2O_4$ Calculated %: Si 14.97
Found ester value: 300.5; 308.0
$C_{18}H_{38}Si_2O_4$ Calculated ester value: 299.4

VII. Bis(trimethylsilyl) Azelaate

A mixture of 65 g (0.6 mole) of chlorotrimethylsilane and 38 g (0.2 mole) of azelaic acid was heated for 92 hours. As a result of treatment similar to that used in the two preceding experiments, an ester of b.p. 180-181°/23 mm was isolated.

Found %: Si 16.0
$C_{15}H_{32}Si_2O_4$ Calculated %: Si 16.84
Found ester value: 347.0
$C_{15}H_{32}Si_2O_4$ Calculated ester value: 336.3

VIII. Bis(triethylsilyl) Azelaate

A mixture of 45 g (0.3 mole) of chlorotriethylsilane and 20 g (0.1 mole) of azelaic acid was heated for 54 hours. After three fractionations at reduced pressure and freezing out under conditions used in previous experiments, 25 g (54%) of ester, b.p. 240-241°/22 mm, was isolated.

Found %: Si 12.76; 12.67

$C_{21}H_{44}Si_2O_4$ Calculated %: Si 13.43

Found ester value: 282.0; 286.0

$C_{21}H_{44}Si_2O_4$ Calculated ester value: 269.2

SUMMARY

1. By direct reaction of trialkylchlorosilanes with saturated mono- and di-basic acids the syntheses have been effected of eight organosilicon esters that have not been described previously in the literature; they include five representatives of the completely unstudied class of esters of dibasic acids.

2. It has been established that most of the synthesized esters are readily hydrolyzed, even by the moisture of the air, a particularly marked tendency to undergo hydrolysis being possessed by esters containing trimethyl-silyl radicals.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 51. INVESTIGATION OF THE POLYESTER EXCHANGE
REACTION BY THE USE OF DEUTERIUM

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As one of us in conjunction with other investigators has established [1], the process of polycondensation cannot be completely described solely in terms of reactions between terminal functional groups. In addition to these reactions which lead to chain growth, others, mainly of a degradational character, occur, these being associated with the presence in the polycondensation products of bonds that may be readily broken under the influence of the starting substances and of other substances of similar chemical nature. In the case of polyesterification, such degradational reactions include acidolysis and glycolysis [2]. alcoholysis [3], and transesterification at the expense of ester linkages [4]. In the case of polyamides, such degradational reactions must be considered to include acidolysis [5, 6], aminolysis [6] and transamidation [7].

The acidolysis reaction of a polyester has been investigated by one of us in conjunction with Golubev [2], the example taken being the reaction of polyethylene adipate with adipic acid. It was found that the degree of degradation was directly proportional to the amount of acid taken for acidolysis. A similar picture was observed previously by one of us in conjunction with Rafikov [5] and Zamyatina [6] in investigations of the acidolysis of polyhexamethylene adipamid by adipic acid.
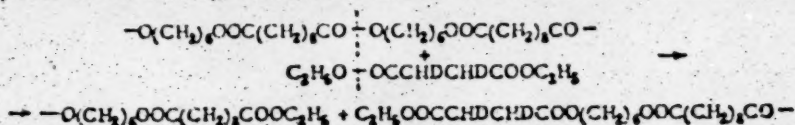
The alcoholysis of a polyester was investigated by one of us and Golubev, the example taken being the reaction of polyethylene adipate with ethylene glycol; a lowering of the molecular weight of the polyester was found to occur [2]. The laws of the alcoholysis reaction were established particularly clearly by Korshak and Vinogradova for the alcoholysis of polyhexamethylene sebacate in presence of hexadecyl alcohol [3]. Flory [8] examined the alcoholysis of two polyesters differing in molecular weight and having terminal hydroxyl groups. He found that in this case also lowering of the molecular weight of the mixture occurred.

The kinetics of the acidolysis and alcoholysis reactions were investigated by two of us with the aid of model reactions of a similar type in which low molecular weight substances [9,10] were used. Acidolysis was investigated for ethyl stearate in acetic acid [9], and it was found that at 250° about 44% of the ethyl stearate taken underwent acidolysis. The alcoholysis of ethyl stearate with hexadecyl alcohol (and also the acidolysis reaction) is greatly accelerated by rise in temperature, and at 183° equilibrium is established when 61.5% of the original ethyl stearate has been converted into hexadecyl stearate [10]. In the alcoholysis reaction the process is greatly accelerated by acids, alkalis, and certain metal salts, whereas alcoholysis is only slightly accelerated by addition of acids [9,10].

Apart however from such exchange reactions, in which the end groups take part, it is possible also for different polymer molecules to react with one another at ester, amide, and other sufficiently polar links [11]. Such reactions must also be degradational, and their role in the general balance of the polycondensation process may evidently be a very important one [12]. However, nobody has yet succeeded in proving the presence of such side reactions experimentally, and any discussion of their significance in the general process must therefore be tentative. The suggestion that such reactions are of considerable importance was made by one of us a considerable time ago [13]. A kinetic investigation of an exchange reaction of this type was carried out by two of us [14]. It was found that the reaction investigated, the transesterification of ethyl stearate and hexadecyl acetate, is greatly accelerated in precence of acid catalysts; alkaline catalysts are somewhat less active. The reaction may occur also in absence of catalyst, but the percent conversion is then considerably lower: Thus in six hours at 183° the degree of conversion was 54.5% in presence of sulfuric acid, but only 13.5% in absence of catalyst.

The present investigation was carried out with the object of obtaining direct experimental proof of the occurrence of exchange (transesterification) reactions proceeding at ester groupings in the course of the polycondensation process. We decided to adopt a new method for this purpose: it consisted in the use of compounds containing a labeled atom, namely deuterium. For our labeled compound we chose diethyl succinate-2,3-d_2, which we caused to react with polyhexamethylene sebacate. Investigation of the products of this reaction could be expected to give an un-

equivocal answer to the question of whether or not there was any interaction involving ester linkages, between the two esters. If the polyester isolated after the reaction with diethyl succinate–2,3-d_2 were found to contain deuterium, it could be regarded as proved that an exchange reaction had occurred in accordance with the following equation:

$$-O(CH_2)_6OOC(CH_2)_8CO + O(CH_2)_6OOC(CH_2)_8CO-$$

$$C_2H_5O + OCCHDCHDCOOC_2H_5$$

$$\rightarrow -O(CH_2)_6OOC(CH_2)_8COOC_2H_5 + C_2H_5OOCCHDCHDCOO(CH_2)_6OOC(CH_2)_8CO-$$

It would be necessary, however, to make sure that unchanged diethyl succinate–2,3-d_2 was completely removed from the polyester, for only then would the answer obtained to our question be unequivocal. On this account a special procedure was evolved for the purification of the polyester, and this ensured that it was almost completely freed from diethyl succinate–2-d_2.

EXPERIMENTAL

Starting Materials

Diethyl Succinate–2,3-d_2. Diethyl succinate–2,3-d_2 was prepared by hydrogenation of diethyl maleate in ethyl acetate solution with deuterium-enriched hydrogen in presence of a palladium catalyst. The heavy hydrogen required was obtained by electrolysis of an alkaline solution of deuterium oxide in water. A solution of caustic soda (1.2 g) in distilled water (2 ml) was placed in a U-shaped electrolysis vessel, and 2 ml of deuterium oxide was added. A current of not greater than 0.5 amp was used. The deuterium-rich hydrogen obtained was collected in a gas holder which was filled with a dilute solution of copper sulfate in distilled water (the solution was pale blue).

Diethyl maleate (10.6g) and ethyl acetate (15 ml) were introduced into a hydrogenation flask, and about 1 ml of a palladium catalyst, prepared by a well known method [15], was added. The air in the flask was displaced with ordinary hydrogen, and the flask was then connected with the gas holder containing deuterium-rich hydrogen. A Drechsel vessel containing sodium plumbite was placed between the gas holder and the flask. The flask was shaken mechanically during the hydrogenation, which was continued until absorption of the hydrogen had completely stopped (about five hours). The total amount of hydrogen absorbed was about 1.5 liters, which was only slightly greater than the amount theoretically required. When absorption of hydrogen had stopped, the catalyst was filtered off and washed with a little fresh ethyl acetate: the filtrate was vacuum-distilled, the fraction boiling at 94–95°/6mm being collected. The product was 15 g (84.6%) of diethyl succinate–2,3-d_2. The deuterium content of the ester was determined by burning it and measuring the density of the resulting water by the float method. The density excess of the water was found to be 3000γ, which corresponds to a 21% deuterium content in the diethyl succinate–2,3-d_2 obtained; hydrogen, for this purpose, being treated as one C–H bond formed in the hydrogenation process.

Polyhexamethylene Sebacate. 1,6-Hexanediol (10g) and sebacic acid (20.54 g, a 20% excess) were placed in a condensation tube and heated in a current of nitrogen, previously purified from oxygen. The temperature was gradually raised: the first seven hours at 180°, after which the temperature was raised to 256° in the course of nine hours. A vacuum of 2–3 mm was applied, and the reaction mixture was maintained at this same temperature for 35 hours. In order to purify the polyester obtained, it was dissolved in benzene and, after filtration of the solution, precipitated with petroleum ether. The polyhexamethylene sebacate obtained had a molecular weight, determined from its viscosity in benzene solution, of 3400. End-group determinations showed that all the end groups were carboxyls.

Method of Investigation and Results

A very important question, which had to be settled before proceeding to the main investigation, was the possibility of completely removing diethyl succinate–2,3-d_2 from the polyester after the reaction. It was essential to be absolutely sure that the whole of the unchanged diethyl succinate–2,3-d_2 could be removed from the polyester, and that the polyester would not retain any in the adsorbed state. Only then could we draw any conclusions on the basis of determinations of deuterium content of the polyester after its reaction with the low-molecular-weight ester.

With this object a weighed amount of the polyester was melted and mixed with a weighed amount of diethyl succinate–2,3-d_2. The homogeneous mixture obtained was subjected to various treatments in order to remove diethyl succinate–2,3-d_2, and the polyester, purified in one way or another, was carefully dried. It was then burnt, and the resulting water was collected and its density excess was determined.

The possibility of effecting purification by repeated extraction of the polyester with ether was tried: A mixture obtained from 1.75 g of polyester and 0.54 g of diethyl succinate-2,3-d_2 was washed repeatedly with ether and was then left overnight under a layer of ether. On the next day the polyester was filtered off, dried and burned. The density excess of the water obtained was 360 γ ; this method of purification was therefore ineffective. Purification by reprecipitation of the polyester was found to be more effective: a mixture obtained from 2 g of polyester and 0.8 g of diethyl succinate-2,3-d_2 was dissolved in benzene and precipitated with petroleum ether, the operation being repeated five times (in experiments in which only three precipitations were given, the density excess of the combustion water was 45 γ); the polyester was then repeatedly shaken with ether over a period of three days, and was then filtered off and burned. The density excess of the combustion water was 30 γ, i.e. in this case practically complete purification of the polyester from diethyl succinate-2,3-d_2 had been effected. This purification technic was applied by us in the isolation of the polyester after reaction with diethyl succinate-2,3-d_2. It should be noted that these experiments have indicated how tenaciously low-molecular-weight impurities may be held in macromolecular compounds and have shown that extraction is a completely unreliable method for the removal of such impurities.

Experiments on the exchange reaction of polyhexamethylene sebacate with diethyl succinate-2,3-d_2 were carried out as follows: polyhexamethylene sebacate (4.02 g) and diethyl succinate-2,3-d_2 (2.46 g) 1 mole per basal mole (per unit link) of polyester, $[-O(CH_2)_6OOC(CH_2)_8CO-]$ were placed in an ampoule, which was freed from air by repeated blowing with nitrogen followed by evacuation. The ampoule was then sealed off and placed in the vapors of boiling biphenyl (b.p. 250°). Heating was continued for ten hours. The reaction product was purified by the five-fold precipitation method already described, and was then burned. The density excess of the combustion water was found to be 347 γ. In a second experiment, carried out under the same conditions, the density excess of the combustion water was 354 γ. The mean density excess of the combustion water was 350 γ.

The presence of deuterium in the polyester after the reaction, which is indicated by the appreciable density excess of the combustion water, is an indisputable proof that an exchange reaction, involving the ester linkages occurs between polyhexamethylene sebacate and diethyl succinate-2,3-d_2, since only in that case could the deuterated ester enter into the composition of the polyester, i.e. be found in the chemically bound state and therefore not be separable by physical methods. As control experiments have shown that a very small amount of diethyl succinate 2,3-d_2 will nevertheless be retained by the polyester, as may be seen from the density excess of 30 γ found in these experiments, it must be assumed that an equivalent density excess of 320 γ for the polyester after reaction will characterize the extent of the exchange that occurred between the polyester and diethyl succinate-2,3-d_2. If complete (100 %) exchange had occurred, the density excess of the combustion water of the polyester after reaction would have been 1000 γ. In our case, therefore, about 30 % of the polyester entered into the exchange reaction with diethyl succinate-2,3-d_2.

SUMMARY

1. An investigation has been made of the exchange reaction between polyhexamethylene sebacate and diethyl succinate-2,3-d_2.

2. It has been proved that exchange reactions involving ester linkages occur during the course of the polyesterification process.

3. A convenient method has been developed for the preparation of diethyl succinate-2,3-d_2.

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RELATIVE BASICITIES OF NITROGEN ATOMS IN COMPOUNDS OF THE
## 2-AMINOPYRIDINE AND 1-ALKYL-2(1H)-PYRIDONIMINE TYPES

Ya. L. Goldfarb, M. A. Pryanishnikova, and K. A. Zhukova

One of the distinguishing characteristics of compounds of the 2-aminopyridine (I) and 1-alkyl-2(1H)-pyridonimine (1-alkyl-1,2-dihydro-2-aminopyridine) (II) types, as systems containing the amidine grouping, is that in their stable salts they function as monoacid bases.
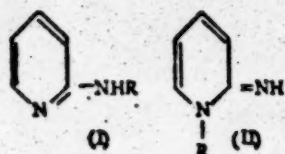

Thus, the molecule of the potentially diacid base (I or II) is able to hold firmly only one proton. This phenomenon, as such, has been satisfactorily explained with the aid of the concept of inductive inactivation [1], but the question of which of the two nitrogen atoms plays the part of the salt-forming center could not be regarded as solved until recently.

In 1947 one of the authors of this communication, together with Setkina and Danyushevsky, concluded on the basis of the results of absorption-spectra studies [2, 3] that in salts of compounds of Type I the proton is bound to the ring nitrogen (the example studied was a salt of 2'-aminonicotine). This conclusion was based on the following experimental results: a) the absorption maximum of 2-aminopyridine (I) is displaced toward the long waves in comparison with that of pyridine by about 400 Å; and b) the absorption curves of the methiodide of 2-dimethylaminopyridine (III)
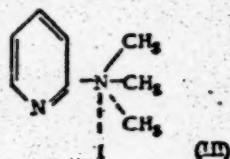
and pyridine are practically identical with respect to the positions of their absorption maxima, and similar coincidence of the curves is observed also for the pair —methiodide of aminopyridine (IV) and 2-aminopyridine (I):
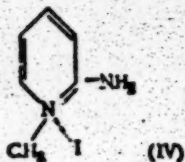
It follows from these facts that salts belonging to the types (V) and (VI)
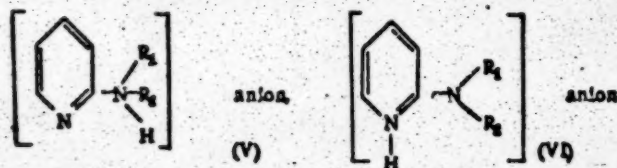
(R₁ and R₂ may be H) should be quite distinct from one another in their absorption spectra, since the first (V) having a quadrivalent side-chain nitrogen is an analog of the methiodide (III), whereas the second (VI) is an analog of the methiodide IV.
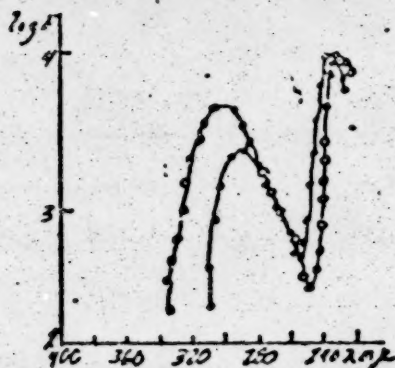

Fig. 1. •–•–•– 2-aminopyridine in heptane; o–o–o–the same in 0.04 N hydrochloric acid.

The hydrochloride of 2'-aminonicotine, which is a substituted 2-aminopyridine, differs insignificantly spectrally from 2'-aminonicotine itself [3]. It was this fact that served as a basis for the above-mentioned conclusion concerning this salt.

The absorption spectra of unsubstituted 2-aminopyridine, as will be seen from our results (see Table 1) and results obtained from the literature, • have the same character in a number of nonaqueous solvents, and when these are replaced by dilute hydrochloric acid, only an insignificant bathochromic shift is to be observed (Fig. 1). Since in this case also there is no displacement toward the short waves when salt formation occurs, the inferences made for 2'-aminonicotine can be extended also to 2-aminopyridine: the salt-forming center is again the ring nitrogen. In these respects the properties of 2-aminopyridine are repeated by derivatives having substituents in the amino group, i.e.: 2-methylaminopyridine and 2-benzylaminopyridine (Figs 2 and 3).
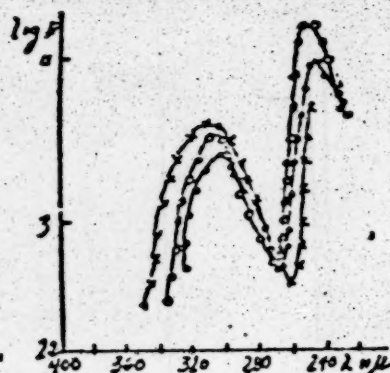
It may be considered that the tendency for the proton to be bound by the ring nitrogen atom will be found in the majority of the bases of Type 1 (R=H, alkyl, or aralkyl), departures from this rule being, of course, possible when certain steric factors operate.

Compounds of Type II are stronger bases than those of Type I. This is shown, in particular, by the fact that the former, in contrast to the latter, form carbonates that are stable at ordinary temperature [4]. The very fact of the change in basicity observed for every pair of isomeric bases (I and

Fig. 2. •–•–•– 2-methylaminopyridine in heptane; o–o–o– the same in dioxane; x–x–x– the same in 0.04 N hydrochloric acid.

Fig. 3. •–•–•–2-benzylaminopyridine in 0.04 N hydrochloric acid; o–o–o– the same in dioxane

II) may be regarded as evidence that a new salt-forming center has arisen. Such a view was in fact advanced by Goldfarb and Danyushevsky [4], who considered that the salt-forming center in bases of Type (II) was at the doubly-bound side-chain nitrogen. The experimental results of the present investigation confirm this point of view.

As will be seen from the results given in the table, these systems differ spectrally from systems of Type (I) in that their absorption maxima preserve their positions in each of the two groups of solvents (heptane, dioxane and ether; ethanol, water, hydrochloric acid), but are appreciably displaced when a solvent of the first group is replaced by one of the second. Setkina, Danyushevsky, and Goldfarb, studying for the first time the absorption

• The results of other authors are distinguished by the insertion of a source reference number in the seventh column of the table.

TABLE

Substance	Formula	max₁ λ (mμ)	Log E	max₂ λ (mμ)	Log E	Reference

| Substance	Formula	$\max_1$ λ (mµ)	Log E	$\max_2$ λ (mµ)	Log E	Reference
2-Aminopyridine:	NH_2					
in heptane		290	3.4	234	4	
in ether		298	~3.6	–	–	[5]
in dioxane		296	3.5	238	4.1	
in dioxane + water *		295	3.7	238	4.1	
in ethanol		293	3.6	–	–	[2]
in 0.04 N hydrochloric acid		301	3.7	233	3.9	**
2-Methylaminopyridine	$NHCH_3$					
in heptane		298	3.4	244	4	
in ether		300	3.7	–	–	[5]
in dioxane		303	3.5	245	4.2	
in dioxane + water		305	3.3	245	4.2	
in ethanol		306	3.6	–	–	
in 0.04 N hydrochloric acid		305	3.6	–	–	
in water		302	3.4	238	4.0	
1-Methyl-2(1H)-pyridonimine	NH, CH_3					
in heptane		346	3.2	257	3.8	
in ether		350	3.5	–	–	[5]
in dioxane		345	3.3	255	4.1	***
in dioxane + water		346:	3.3	250	3.8	***
		302	3.4	–	–	
in 0.04 N hydrochloric acid		299	3.6	–	–	[3]
in ethanol		300	3.9	–	–	
2-Benzylaminopyridine	$NHCH_2C_6H_5$					
in dioxane		306	3.4	247	4	
in dioxane + water		307	3.5	246	4	
in 0.04 N hydrochloric acid		309	3.7	238	4.1	
1-Benzyl-2(1H)-pyridonimine	NH, $CH_2C_6H_5$					
in heptane						
in dioxane		350	3.4	255	3.7	
in dioxane + water		353	3.5	257	3.8	
in 0.04 N hydrochloric acid		305	3.6	237	3.8	
		300	3.7	–	–	
1-(2-Hydroxyethyl)-2(1H)-pyridonimine	NH, CH_2CH_2OH					
in dioxane						
in dioxane + water		350	3.5	258	4	
in ethanol		305	3.6	235	3.7	
in 0.04 N hydrochloric acid		305	3.6	236	3.7	
in water		302	3.7	–	–	
		303	3.6	238	3.6	
1-Methyl-6-(1-methyl-2-pyrrolidinyl)-2(1H)pyridonimine	NH, CH_3, CH_3					
in heptane						
in dioxane		350	3.5	256	4	
in dioxane + water		350	3.6	258	4	
in 0.04 N hydrochloric acid		305	3.7	240	3.7	
in water		310	3.7	235	3.8	
		305	3.7	234	3.7	

* Dioxane 70%, water 30%.

** See also [9].

*** See also [5].

spectra of some bases of the 1-alkyl-2(1H)-pyridonimine type, observed a similar type of displacement when comparing the absorption curves for 1-methyl-2(1H)-pyridonimine in heptane and in alcohol [2], and later Anderson and Seeger observed a similar phenomenon when comparing the absorption spectra of this base in anhydrous and in aqueous dioxane [5].

In connection with the question under examination, it must be pointed out here that the absorption curves of pyridonimine systems in acid media are practically identical, with respect to the positions of the maxima, to the absorption curves of aminopyridine systems (Fig. 4, 5, and 6). This may be interpreted as due to the reaction of the former with acid to give the structure of the second (aminopyridine) type:


(VII)
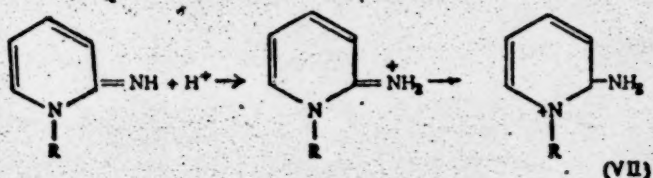
It will be seen that it is suggested in this scheme that the proton unites with the side-chain nitrogen atom, yielding, owing to simultaneous displacement of the double bond, a compound having the benzene bond system. If the proton had added at the ring nitrogen, an ion would have been formed of structure
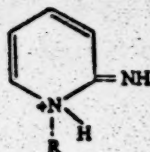
having the same system of bonds as that of the original compound (Type II) and spectrally not distinguishable from it. Actually, compounds of structure II in heptane or dioxane give a band having a maximum at 3450-3500 A, whereas in acid the maximum is at about 3000 A.

From these results we may conclude that the side-chain nitrogen atom in molecules of bases of Type (II) has a greater affinity for a proton than the ring atom, and, since the affinity for a proton is the criterion for the strength of the base, we may speak of the relative or comparative basicity of these two atoms. It is relevant here to note the parallelism in properties between 1-alkyl-2(1H)-pyridonimines and simple amidines: in the latter also, according to Shigorin and Syrkin's results [6], the more basic nitrogen atom is the double-bound imine atom. The higher basicity of the side-chain nitrogen of compounds of Type(II) is evidently related to some extent to the tendency of the ion formed by addition of a proton at this point to pass into the energetically favored benzenoid system (see equation above).

In view of the fact that the absorption curves for 1-benzyl-2(1H)-pyridonimine and the isomeric 2-benzylaminopyridine, dissolved in each case in ethanol, are found to be coincident [3] and that the same applies to another pair of isomeric bases, 1-methyl-2(1H)-pyridonimine and 1-methylaminopyridine (see table and [2]), we may conclude that the same transformation occurs also when bases of Type II react with ethanol. The structure of the system formed (VIII)

(VIII)
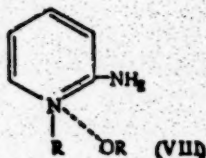
should not differ spectrally from that of bases of Type (I) or of the salts of the structure (VII); this is found to be so when the relevant curves are compared (see the table and the curves in Fig. 7).

The coincidence of the absorption curves of aminopyridine and pyridonimine systems in alcohol and, as we shall see, in water may therefore be explained by the interaction of a base of the second type with the

medium. In this connection, it should be noted that the explanation of the spectral identity of compounds of Types (I) and (II) given in the paper by Goldfarb, Danyushevsky, and Setkina [2,3] was incorrect, being based on a concept concerning the superposition of structures that is known to be erroneous; as we have seen, the absorption spectra of bases of the second type in media that do not react with them (dioxane, heptane, etc.), differ greatly from those of the 2-aminopyridine series.

From the results given in the table and the curves in Figs. 5, 6, 7, and 8, it will be seen that substituted 2(1H)-pyridonimines (II) give absorption bands that are characteristic for 2-aminopyridine systems also in the cases in which water or aqueous dioxane is used as solvent. 1-Methyl-2(1H)-pyridonimine in aqueous dioxane, as was shown by Anderson and Seeger [5] and has been confirmed by us, gives not only the band corresponding to the 2-aminopyridine type of system, but also its own characteristic band with a maximum at 3450 A. In this case, therefore, we have an equilibrium system [5]:
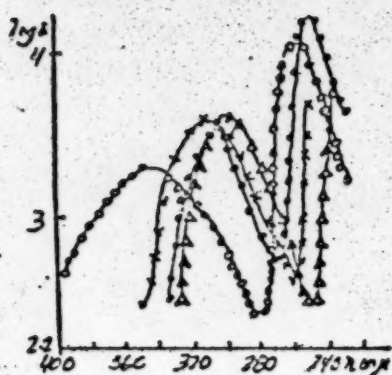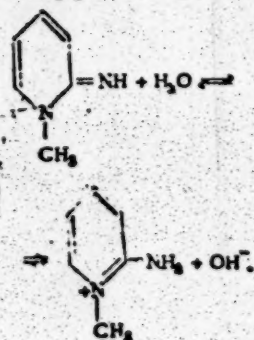

Fig. 4. ●—●—●— 2-methylaminopyridine in dioxane; x—x—x— the same in 0.04 N HCl; o—o—o— 1-methyl-2(1H)-pyridonimine in dioxane; Δ—Δ—Δ— the same in 0.04 N HCl.
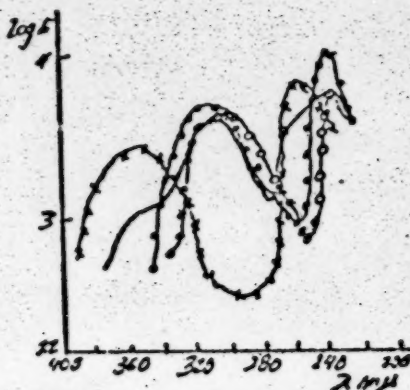

Fig. 5. x—x—x— 1-benzyl-2(1H)-pyridonimine in dioxane; o—o—o— the same in 0.04 N HCl; —— the same in dioxane + water; ●—●—●— 2-benzylaminopyridine in 0.04 N HCl.
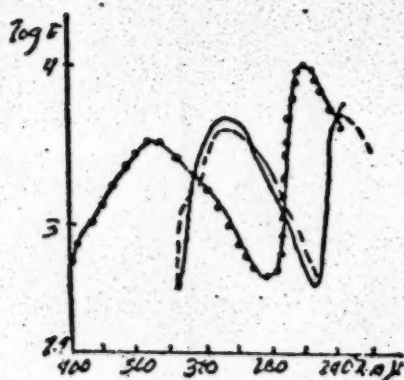

Fig. 6. ●—●—●— 1-(2-hydroxyethyl)-2(1H)-pyridonimine in dioxane; —— the same in dioxane + water; ——— the same in 0.04 N HCl.
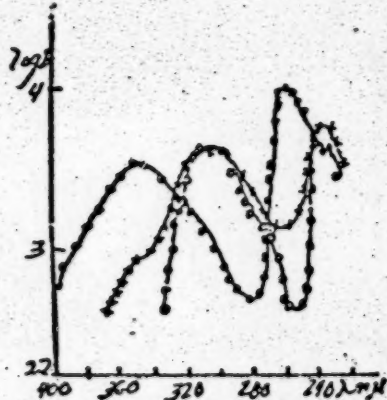

Fig. 7. ●—●—●— 1-(2-hydroxyethyl)-2(1H)-pyridonimine in dioxane; x—x—x— the same in ethanol; o—o—o— the same in water.

The first, long-wave maximum, corresponding to systems of Type (II), is not found in all cases; this may be because the equilibrium is strongly displaced toward the aminopyridine structure.

When 2-aminopyridine reacts with ethylene oxide in alcohol [7] or in aqueous dioxane [8], 1-(2-hydroxyethyl)-2(1H)-pyridonimine is formed. In absence of water or alcohol, this reaction does not go [8]. Taking this

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fact into account and assuming also that 2-aminopyridine reacts only in the aminopyridine form [2], Goldfarb and Pryanishnikova have suggested [8] the following scheme for the mechanism of the formation of this base:
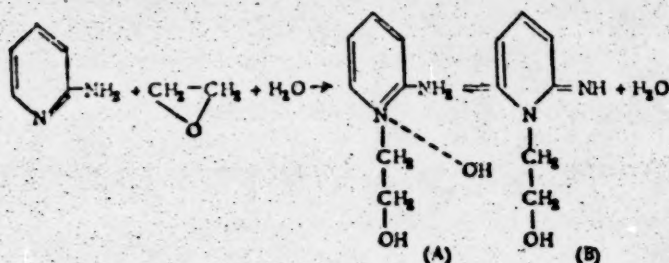
An attempt to isolate the base (A), as such, could not, of course succeed; it was therefore necessary, in order to confirm that it was possible for the process to proceed according to this scheme, to make sure that the base (B) was able to give, by hydration, a quaternary base of structure (A). The results given in the table and by the curve in Fig. 7, provide evidence in support of the view that in solvents of the water type, 1-(2-hydroxyethyl)-2(1H)-pyridonimine,

Fig. 8. $\bullet-\bullet-\bullet-$ 1-Methyl-3-(1-methyl-2-pyrrolidinyl)-2(1H)-pyridonimine in dioxane; $x-x-x-$ the same in dioxane + water, $o-o-o-$ the same in 0.04 N HCl.

which gives a band that is characteristic for aminopyridine systems, reacts with the solvent forming a quaternary base of the type (A).

EXPERIMENTAL

1. Chemical Part of the Work

2-Methylaminopyridine was prepared by the method of Chichibabin and Knunyants [10]; it had a b.p., after two distillations, of 92°/11 mm. 1-Methyl-2(1H)-pyridonimine, b.p. 90°/6 mm, was prepared by the method of Chichibabin, Konovalova and Konovalova [11].

2-Benzylaminopyridine was prepared by the method of Chichibabin and Knunyants [12]. The product was recrystallized twice from alcohol and then melted at 84°. 1-Benzyl-2(1H)-pyridonimine, b.p. 169°/6 mm, was synthesized by the method of Chichibabin, Konovalova, and Konovalova [11]. 1-(2-Hydroxyethyl)-2(1H)-pyridonimine was obtained by Knunyants' method [7]. The substance was crystallized three times from absolute alcohol, and then melted at 127.5—128.5°.

1-Methyl-3-(1-methyl-2-pyrrolidinyl)-2(1H)-pyridonimine was prepared by Goldfarb and Kordakova's method [13] and was purified via the carbonate. After being liberated from this salt, it was again vacuum-distilled, b.p. 144-147°/3 mm. 2-Aminopyridine was purified by vacuum distillation and recrystallization from heptane: m.p. 57-58°.

The solutions required for the spectrum determinations were prepared under conditions that excluded the entry of carbon dioxide and moisture from the air. Weighed amounts of the pyridonimines were taken in micro-capillaries, which were then broken under the solvent, the air in the flask having been previously displaced by nitrogen.

2. Optical Part of the Work

The spectra were photographed on a medium-sized Hilger spectrograph. The dispersion of the spectrograph was 44 mμ/mm at 360 mμ, and 12 mμ/mm at 250 mμ. The light source was a tungsten arc. The dimensions of the slide of the spectrograph were 13 x 18 cm, and isoortho plates, sensitivity 400, were used. The developer was of the metal-hydroquinone type, and the fixing bath was acid. The spectra were measured by the "equal blackening" method. A quartz Hufner rhomb served for dividing the light beam. Variation in the intensity of the comparison beam was effected with the aid of a rotating sector. The places of equal blackening were found visually. The wavelength scale was provided by the spectrum of a copper arc. Every spectrum was measured several times, and the result was considered to be satisfactory when the points found from the last
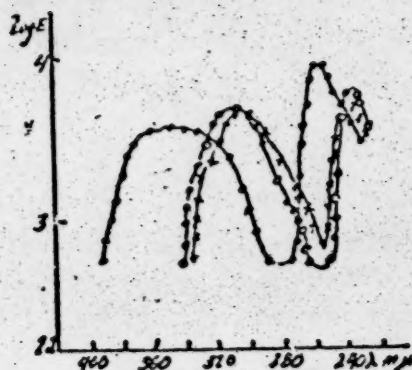
photograph of the spectrum fitted closely to the curve obtained from previous photographs. The concentration of the solution of a compound investigated was altered by factors of 10 and 100.

We feel that it is our duty to express our deep gratitude to Prof. E. V. Shpolsky for making it possible for us to carry out the optical part of the work in the optical laboratory of which he is director; also for his interest in our work.

SUMMARY

1. It has been shown, by comparison of the absorption spectra of compounds of the 2-aminopyridine series and the 2(1H)pyridonimine series in various media, that the salt-forming center in bases of the first type is to be found at the ring nitrogen atom, whereas in bases of the second type it is to be found at the side-chain nitrogen.

2. When substituted 2(1H)pyridonimines are dissolved in dilute acid or in alcohol (or water [5]), they assume structures of the 2-aminopyridinium salt type.

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RELATION BETWEEN THE STRUCTURES OF CERTAIN ORGANIC BASES AND THEIR ABILITY TO FORM ADDITION COMPOUNDS WITH CARBONIC ACID

COMMUNICATION 2. PYRIDINE DERIVATIVES

Ya. L. Goldfarb and Ya. L. Danyushevsky

The results of a study of the action of carbonic acid on certain nicotine derivatives, which were presented in the first communication [1] led us to the following conclusions: 1) bases having the 2(1H) pyridonimine (1,2-dihydro-2-iminopyridine) system of bonds (A) are precipitated from their solutions in ether or acetone by carbonic acid, yielding salts relatively stable at room temperature; 2) bases having the isomeric structure (B) are not precipitated from their solutions in these solvents by carbonic acid at room temperature; 3) in the salts mentioned the salt-forming center is at the doubly bound side-chain nitrogen; and 4) the compounds formed by addition of carbonic acid to nicotonimines are carbonates, not carbamates.
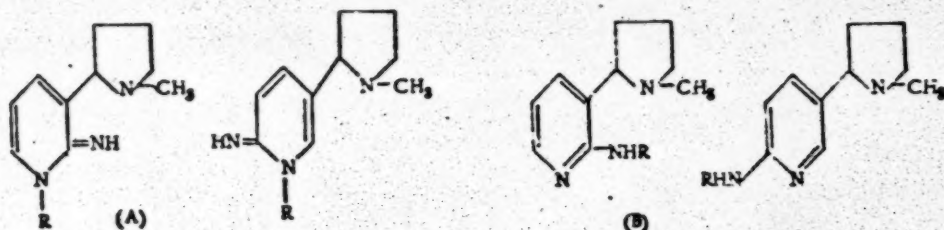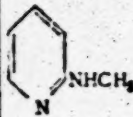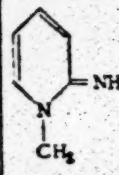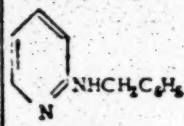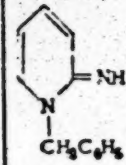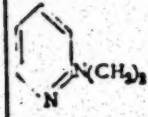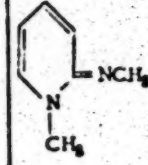

It was considered desirable to determine the extent to which these conclusions applied to analogous compounds of the pyridine series, in which the basic properties are associated with the presence in the molecule of only the two nitrogens of the amidine grouping and are not subject to the influence of the third nitrogen atom that is present in bases of types A and B. The results of the experiments that we accordingly carried out are given in the table; for convenience, they are arranged so that comparisons may readily be made between the members of each pair of isomeric bases with respect to their behavior toward carbonic acid.

Examination of these results shows, first of all, that, as in the case of the corresponding nicotine derivatives, 1-alkyl- and 1-aralkyl-2(1H)-pyridonimines form carbonates that are stable at room temperature. Thus, from a very dilute ethereal solution of 1-methyl-2(1H)-pyridonimine containing the necessary amount of water, precipitation of the salt begins as soon as passage of CO_2 begins; precipitation is about 90% complete* at room temperature, and the yield may be further increased to 94-95% by lowering the temperature to -10-$15°$. 2-Methylaminopyridine (II), which is isomeric to (IIa), is not precipitated at room temperature, even from a relatively concentrated solution; only when the temperature is lowered to -30-$35°$ is a turbidity to be observed in the solution, and a thin layer of oil is formed, which immediately gives up CO_2 to the air. The nature of the product formed in this case, and also that of the crystalline compound formed from 2-aminopyridine (.) at low temperature, could not be established owing to the high instability of these substances. In view of the other results given in the table and in the first communication [1], we may suggest only that these products are not salts of the tautomeric, pyridonimine forms of 2-aminopyridine or 2-methylaminopyridine, since salts of this type are stable at room temperature. The behavior observed for the isomeric pairs of bases (II) and (IIa), and (IV) and (IVa) is similar to that of the pair (II) and (IIa).

2-Benzylaminopyridine (III) is not precipitated by carbonic acid at ordinary temperatures, even from a 3% solution, and when the temperature is lowered the precipitate formed is not a salt, but unchanged base. The

* The yields given in the text relate to the amount of salt obtained by saturation of a solution of the concentration indicated in the table with carbon dioxide.
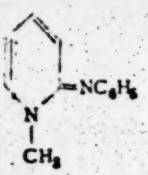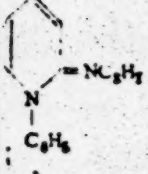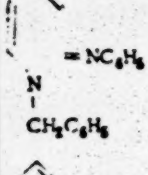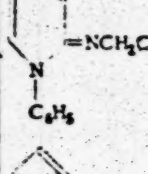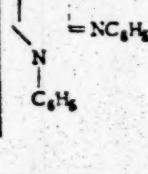
Compound No.	Base	Solvent	Amt. substance per 100 ml of solvent (g)	Limit of lowering temp. (°C)	Precipitation		Stability of addn. prod. at room temp.	Reaction with Ba++	Found (%)		Calculated (%)	
					S	S+H₂O			C	H	C	H
1	2	3	4	5	6	7	8	9	10	11	12	13
(I)	NH₃	E	1.5; 2.0	−40 −50	cr. ppt.	cr. ppt.	unstab.	+				
(II)	NHCH₃	E	20.0	−30 −35	−	oil	unstab.	+				
(IIa)	NH CH₃	E A EA D P	1.0; 2.0 1.0; 2.0 2.0 2.0 2.5	room room room room room	− − − − −	cr. ppt. cr. ppt. ditto ditto ditto	stab. stab. stab. stab. stab.	+ + + + +	44.65 44.72	6.31 6.51	44.68 C₆H₈N₂·H₂CO₃·H₂O	6.38
(III)	NHCH₂C₆H₅	E A	1.0; 3.0 10.0	−15 −25 −5	− −	orig. base −						
(IIIa)	NH CH₂C₆H₅	E A	1.5; 4.0 1.5	room room		cr. ppt. cr. ppt.	stab. stab.	+ +	63.07 63.44	5.73 5.78	63.41 C₁₂H₁₂N₂·H₂CO₃	5.69
(IV)	N(CH₃)₂	E E and A 1:1	3.0 14.0	−50 −50	− −	− −						
(IVa)	NCH₃ CH₃	E A	1.6 1.3	room room	− −	cr. ppt. ditto	stab. stab.	+ +	47.23 47.56	6.89 6.71	47.52 C₇H₁₀N₂·H₂CO₃H₂O	6.93

* See page 140 for footnote and key to abbreviations.

1	2	3	4	5	6	7	8	9	10	11	12	13
(V)	pyridine ring with =NCH₂C₆H₅ and N-CH₃	E	1.7; 2.0	room	–	cr. ppt.	stab.	+	60.30 60.52	6.33 6.50	60.43 $C_{13}H_{14}N_2 \cdot H_2CO_3 H_2O$	6.47
		A	1.5; 5.0	0–10	–	ditto	stab.	+				
(VI)	pyridine ring with =NH and N-CH₂-CH₂-OH	A	1.1	room	–	ditto	stab.	+	48.23 48.31	6.08 6.14	48.00 $C_7H_{10}N_2O \cdot H_2CO_3$	6.00
(VII)	pyridine ring with N-CH₃ and COC₆H₅	E	14.6	−40 −50	–	orig. base						
		A and E 2:1	7.0	−50	–	–						
(VIII)	pyridine ring with -NHC₆H₅	A	7.0	−35	–	orig. base						
(IX)	pyridine ring with =NCOCH₃ and N-CH₃	E	1.0	+3 – +5	–	oil	unstab.	+				
		A	6.0	−30 – −45	–	oil	unstab.	+				
(X)	pyridine ring with =O and N-CH₃	A	10.0	−50	–	–						
		E and A 1:1	5.0	−50	–	–						
(XI)	pyridine ring with =NC₂H₅ and N-C₆H₅	E		−10 −12	–	oil	unstab.	+				
(XII)	pyridine ring with =NC₆H₅ and N-C₂H₅	E	10.0; 20.0	−35	–	mixture of oil and cr. ppt.	unstab.	+				

TABLE -- (continued)

1	2		3	4	5	6	7	8	9	10	11	12	13
(XIII)	(structure: pyridine ring, =NC$_6$H$_5$, N–CH$_3$)		E	1.5; 2.0	−25 −40		cr. ppt.	stab.	+	62.16	6.14	63.41	5.69
			A	1.0; 8.0	−25 −40		ditto	stab.	+	61.89	6.07	C$_{13}$H$_{13}$N$_2$·H$_2$CO$_3$	
(XIV)	(structure: pyridine ring, =NC$_3$H$_7$, N–C$_6$H$_5$)		E	1.0	room	−	oil		+				
(XV)	(structure: pyridine ring, =NC$_6$H$_5$, N–CH$_2$C$_6$H$_5$)		E	2.5	−0 −5	−	orig. base						
			E and A 3:1	2.5	−50		orig. base						
(XVa)	(structure: pyridine ring, =NCH$_2$C$_6$H$_5$, N–C$_6$H$_5$)		E	1.0	room		oil		+				
(XVI)	(structure: pyridine ring, =NC$_6$H$_5$, N–C$_6$H$_5$)		E	1.0	−50		orig. base						
			B and E 2:3	4.0	−40		orig. base						
			A	3.0	−40- −50		orig. base						

* For information concerning apparatus and procedure see the first communication [1]. The concentrations of the solutions were chosen so that the aminopyridine base was treated under the more favorable conditions for precipitation; in some cases, however, it was not possible to obtain a solution of the desired concentration, owing to the limited solubility of the base. The amount of water introduced was 1.2 moles per mole of base. At low temperature a part of it froze out, but this did not affect the course of the precipitation. The time during which carbon dioxide was passed varied from 30 minutes to several hours, depending on the observed rate of precipitation.

Abbreviations: S, dry solvent; E. ether; A, acetone; D, dioxane; EA, ethyl acetate; P, pyridine; B, benzene; −, does not precipitate; cr. ppt., crystalline precipitate (underlined, rapid precipitation; not underlined, slow precipitation); stab., stable; unstab., unstable, rapidly decomposing in the air with evolution of CO$_2$; +, positive; orig. base, original base.

Isomeric 1-benzyl-2(1H)-pyridonimine, however, begins to be precipitated from its 2% solution in ether already at room temperature; the yield of salt may then reach 30%, but by lowering of the temperature to −10 − −15° the yield may be raised to 95%. 2-Dimethylaminopyridine (IV) is not precipitated from its dilute ether solution, or relatively concentrated ether−acetone solution, even when the temperature is lowered to −50°. The isomeric N^2,1-dimethyl-2(1H)-pyridonimine (IVa) forms a stable salt in 80% yield from ether solution at room temperature; the yield from acetone solution is about 57%.

In this last case, since the possibility of the formation of carbamate is excluded and the addition product is formed with participation of water, it may be regarded as established that it is a carbonate. A similar conclusion can be made on the basis of analogy for other stable carbonic acid addition compounds that are characterized in the table. In this connection it should be noted that these addition products have the characteristic property of being soluble in water.

It will be seen from these considerations that we have treated the nonappearance of a precipitate when the ether solution of a base was saturated with carbonic acid as an indication that the salt was unstable under the given conditions. It may be supposed that in our experiments the main factor determining the behavior observed was the degree of instability of the salt, and not its solubility. Generally speaking, the carbonates of 1-alkyl-2(1H)-pyridonimines are practically insoluble even in moist ether; thus, when the carbonate of 1-benzyl-2(1H)-pyridonimine (IIIa) is heated with ether, only traces of base, formed by decomposition of the salt, pass into solution. The solubilities of the carbonates of the isomeric 2-alkylaminopyridines could not be directly determined, since such salts were not accessible at room temperature. Since, however, compounds of the 2-aminopyridine structure, such as 2-benzylaminopyridine (III), are less soluble in ether than those having the isomeric pyridonimine structure (IIIa), it may be supposed that the ether-solubility of salts of the base (III) will in any case be not greater than that of salts of the base (IIIa). We have seen that at room temperature a salt is precipitated from a solution of 1-benzyl-2(1H)-pyridonimine (IIIa) when it is saturated with carbon dioxide, whereas a solution of (III) remains unchanged under these conditions; the whole course of these considerations, therefore, leads us to the conclusion that the carbonate of 2-benzylaminopyridine is either not formed, or is unstable, at room temperature.

In the light of the above considerations, the relation of the compounds (V, VI, and VII) to carbonic acid becomes clear. The first two compounds, which belong to the 1-alkyl-2(1H)-pyridonimine series, are precipitated from ether or acetone solution with formation of stable carbonates, but the compound (VII), which is an acyl derivative of 2-methylaminopyridine, and the compound (VIII), do not form salts even at very low temperatures.

The presence in the molecule of 2-aminopyridine, or one of its derivatives, of an amidine grouping, is revealed by a number of properties, which permit a clear demarcation to be made between the province of bases of this type and that of bases of the 3-aminopyridine series. It is well known, for example, that stable salts of 2-aminopyridine bases contain one, and not two equivalents of acid. The cause of this phenomenon, according to Mann [2], is to be found in the inductive effect due to the positive charge on the nitrogen attached to the proton of the acid; this explanation, however, leaves open the question of which of the two nitrogen atoms of the 2-aminopyridine system is the salt-forming center. On the basis of a study of the absorption spectra of a number of pyridine and nicotine derivatives, we, with Setkina, concluded that the proton unites to the ring nitrogen atom (the compound for which this was demonstrated was 2'-aminonicotine) [3]. From these and other results [4] it may be shown that the molecule of 1-alkyl-2(1H)-pyridonimine unites with a proton through the side-chain nitrogen atom:
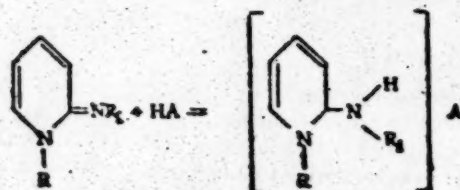
In view of these facts, it was considered to be of interest to examine the behavior toward carbonic acid of a number of substituted 2(1H)-pyridonimines whose main function had been weakened by the introduction of an electronegative radical into the amidine grouping. One of the members of this group, N-acetyl-1-methyl-2(1H)-pyridonimine (IX), is precipitated at low temperature from ether or acetone in the form of an oil, which gives up carbon dioxide at room temperature. Thus, weakening of the basic properties due to introduction of an acetyl group into the 1-methyl-2(1H)-pyridonimine (IIa) molecule is still insufficient to deprive it of the ability to be precipitated by carbonic acid (from an approximately 1% solution in ether) at a temperature close to 0°.

As we have already seen, 1-alkyl-2(1H)-pyridonimines form salts by accepting a proton at the side-chain (not ring) nitrogen atom. One of the causes of this phenomenon is evidently that only this type of addition ensures the formation of a compound having the energetically favorable benzenoid bond system (see the above equation). It is quite possible that this factor plays an important part also in the reaction of acids with 1-alkyl-2(1H)-pyridone, i.e., in this case also, the process is favored by the formation of a stable benzenoid system. It is quite clear that a system

of this type could be obtained simply by the addition of a hydrogen ion at the oxygen atom of the 1-alky-2(1H)-pyridone molecule:
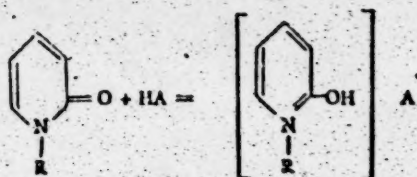
This view of the structure of salts of 1-substituted 2(1H)-pyridone [5] is confirmed by the results of Specker and Gawrosch [6] on the absorption spectra of N- and O-substituted 2(1H)-pyridone. It is of interest in this connection to note that the hydrochloride of 1-methyl-2(1H)-pyridone, like 2(1H)-pyridone [8] shows a coloration with ferric chloride [7, 9].

On the basis of these considerations it was considered desirable to include 1-methyl-2(1H)-pyridone among the compounds to be studied. Actually, the formation of a stable carbonate in this case would serve as a further confirmation of the suggested structure of the salt, although, if the carbonate were found to be unstable, this would not, of course, mean that the formula cited must be regarded as unsatisfactory.

1-Methyl-2(1H)-pyridone has been described as a strong base that absorbs carbon dioxide from the air [7, 9]. Our observations (see the table) are not in accord with such a description of the compound: when its solution in ether or ether—acetone mixture is saturated with carbon dioxide, no turbidity or precipitate is to be observed even when the temperature is lowered to −50°. It is still not clear to us what conditions must be observed for the formation of a salt, as described by Fischer and Chur [9], when carbon dioxide is passed through an ether solution of 1-methyl-2(1H)-pyridone.

Since the salt-forming center of the 2(1H)-pyridonimine molecule is the side-chain nitrogen atom, it may be expected that the effect of an aryl radical (lowering of the stability of the carbonate) will be greater when it is attached to this nitrogen, and not to the ring nitrogen atom. For the compounds that were accordingly examined, 1-ethyl-N²-phenyl-2(1H)-pyridonimine (XII) and N²-ethyl-1-phenyl-2(1H)-pyridonimine (XI), we could not, however, find any notable difference in their behavior toward carbonic acid. In this connection it should be noted that the observation of the tendency of phenyl-substituted 2(1H)-pyridonimines to be precipitated is rendered difficult, in general, by the fact that their addition products with carbonic acid are precipitated very slowly and in the form of oils. An exception in this respect is 1-methyl-N²-phenyl-2(1H)-pyridonimine (XII), which forms a crystalline carbonate that only slowly loses carbon dioxide; the analytical results for this compound are not fully in accord with those calculated from the formula, but the discrepancy is small.

A clearer picture of the effect of the aryl radical is to be observed in the case of two other substituted 2(1H)-pyridonimines, 1-benzyl-N²-phenyl-2(1H)-pyridonimine (XV) and N²-benzyl-1-phenyl-2(1H)-pyridonimine (XVa). The second of these compounds is precipitated from ether solution by carbonic acid in the form of an oily addition product already at room temperature, whereas the first is precipitated unchanged at low temperature.

The effect of a second aryl radical, not directly bound to the side-chain nitrogen of a substituted 2(1H)-pyridonimine, on the stability of the salt may be examined by a comparison of the results of experiments on the action of carbonic acid on 1-methyl-N²-phenyl-2(1H)pyridonimine (XII) and N²-1-diphenyl-2(1H)-pyridonimine (XVI).

In conclusion, the authors consider it necessary to emphasize that, since the stability of the carbonic acid addition products could be determined only approximately and the observation of the course of the precipitation was difficult in a number of cases, the conclusions reached on the basis of the results presented can serve only as a general qualitative characterization of the behavior of substituted 2(1H)-pyridonimines and their isomers of the 2-aminopyridine series toward carbonic acid.

SUMMARY

1. It has been shown that certain substituted 2(1H)-pyridonimines are precipitated at room temperature by carbonic acid from their solutions in ether or acetone.

2. It has been shown that the addition products formed in this way between carbonic acid and the bases are stable at room temperature and are the carbonates of the bases.

3. Bases of the 2-aminopyridine series are not precipitated at room temperature by carbonic acid from their solutions in ether or acetone.

4. The introduction of a phenyl or acetyl radical into the amidine grouping of 1-methyl (or benzyl)-2(1H)-pyridonimine does not lead to loss of the ability of the compound to be precipitated by carbonic acid.

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THEORY OF TAUTOMERIC EQUILIBRIUM

COMMUNICATION 3. THE QUESTION OF PSEUDOMERISM. STRUCTURE AND PROPERTIES OF DIALKYL THIOPHOSPHITES

### M. I. Kabachnik and T. A. Mastryukova

I

One of us has recently shown that prototropic tautomeric equilibrium belongs to the protolytic acid-base type. In equilibrium there are two acids, which both give the same anion, and a solvent or other base present in the solution is the carrier of the proton. The tautomeric equilibrium constant is the ratio of the ionization constants of the tautomeric forms in the given solvent S [1, 2].

In the problem of tautomerism the question of the effect of the position and rate of establishment of the equilibrium is of great significance for the course of chemical reactions. In this respect particular interest is presented by equilibrium mixtures for which the position of equilibrium is strongly displaced in one direction; these occur when the forms differ greatly in their ionization constants: the position of equilibrium is displaced in the direction of the less acidic form, and the greater the difference in the ionization constants, the greater the displacement will be.

We have investigated the chemical properties of such a tautomeric pair for the case of dialkyl thiophosphite [dialkyl phosphonothionate (I) and O,O-dialkyl hydrogen phosphorothioate (II):


which were recently synthesized from tetraphosphorus heptasulfide and alcohols [3]. Dialkyl thiophosphites are sulfur analogs of dialkyl "phosphites" (dialkyl phosphonate III and dialkyl hydrogen phosphite IV):
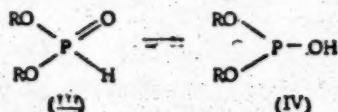
The question of the tautomerism of these and their chemical properties have been studied in detail by many chemists, particularly by A. E. Arbuzov and his students [4]. The general opinion is that the tautomeric equilibrium of the dialkyl phosphites is considerably displaced in the direction of the form (III). As the difference in acidic properties between the tautomeric forms must be greater for the dialkyl thiophosphites than for their oxygen analogs, the equilibrium must be still more displaced in the direction of the phosphonic form (I).

We wished to find chemical reactions of dialkyl thiophosphites that would give an unequivocal indication of the part played in the reaction by the form (II). We presumed that, as this form was consumed in the reaction, the equilibrium would be constantly reestablished, until the whole of the dialkyl phosphite had undergone the reaction characteristic for the form (II). In particular, the form (II) should be responsible for various addition reactions: the addition of sulfur, cuprous halides, alkyl halides, etc., which is so characteristic for tervalent phosphorus compounds [5] and is not in any way peculiar to quinquevalent phosphorus. Dialkyl thiophosphites, however, did not undergo any of these addition reactions. Of those properties that might be ascribed to the presence of the form (II) we found only one: the ability of diethyl thiophosphite to form metal derivatives (sodium, silver), the structure of which is generally accepted to be that of formula (V).
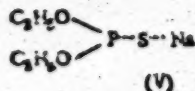
It was found, however, that the sodium salts did not correspond in their behavior toward water to salts of a relatively strong acid, such as the form (II) would be expected to be; they were immediately hydrolyzed by water. The results obtained led us to the conclusion that in this greatly displaced equilibrium, such as the equilibrium (I)⇌(II) must be, the chemical properties of the form (II) are almost completely suppressed, evidently owing to the low value of its effective concentration. This conclusion, however, was in conflict with the generally accepted concept of pseudomerism.

II

The concept of pseudomerism was introduced into science at the end of last century, following the work of Bayer on isatin [6]. It related to the phenomena exhibited by a substance, such as isatin, known in only one form, but forming two series of derivatives, corresponding in structure to two possible tautomeric forms.

Later, when it had been confirmed that tautomerism is nothing more than equilibrium isomerization — a phenomenon discovered by Butlerov [7] long before the appearance of the tautomerism concept — the term "pseudomerism" began to be understood as relating to very much displaced, but rapidly established, tautomeric equilibria, in which the concentration of one of the forms is so low that it cannot be measured by any of the usual chemical or physical methods ("immeasurably low", "vanishingly low", etc., concentrations), but, owing to the high reactivity of this form and the rapidity with which equilibrium is established, this form enters into particular chemical reactions and so forms its own series of derivatives.

This concept of pseudomerism appears to have been introduced by Knorr [8]. It was particularly systematically developed by Ingold and Thorpe [9], and it has received wide acceptance. It has even been suggested that the position of the equilibrium A ⇌ B may be "anywhere" [10] and it will still be possible to treat the conversion of A into B' in terms of the pseudomeric change

$$A \rightleftarrows B \longrightarrow B',$$

It is only necessary to assume sufficiently high rates of conversion.

From a certain time all cases in which a substance is in fact known only in one form but forms two series of derivatives began to be explained by the pseudomerism concept. This extreme point of view is taken in, for example, Baker's book "Tautomerism" [11].

How erroneous this generalization is has been shown by recent investigations by Nesmeyanov, Lutsenko, Sazonova, and others. They have shown that two series of derivatives may be formed when tautomeric relationships are completely absent. For example, α-mercurated aldehydes and ketones having the keto structure (VI)

$$ClHg-\overset{|}{C}H-\overset{|}{C}=O \qquad\qquad \overset{|}{C}H=\overset{|}{C}-OHgCl$$

(VI)   (VII)
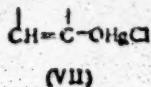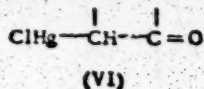
which are not capable of reversible conversion into the mercury derivatives of the corresponding enol forms (VII), are able, depending on the nature of the reagent, to give both C- and O-derivatives, for example (VIII) and (IX) [12]:

$$(C_6H_5)_3C-CH_2-CHO \qquad\qquad CH_2=CH-O-C(C_6H_4NO_2)_3$$

(VIII)   (IX)
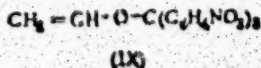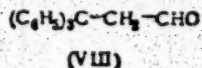
Again, stereoisomeric (cis-trans) magnesium (lithium, sodium) enolates of certain ketones (X and XI) are incapable of reversible conversion into the corresponding organometallic keto forms (XII) (this follows from the fact that the stereoisomers do not undergo interconversion under the conditions studied).

$$\begin{array}{ccc} \overset{H}{\diagdown}\overset{R'}{\diagup} & \overset{R}{\diagdown}\overset{R'}{\diagup} & \overset{H}{\diagdown}\overset{R'}{\diagup} \\ C=C & C=C & C-C \\ \diagup \qquad \diagdown & \diagup \qquad \diagdown & \\ R \qquad OMgX & H \qquad OMgX & R \qquad O \end{array}$$

(X)   (XI)   (XII)
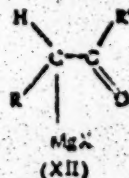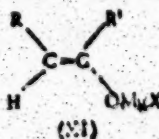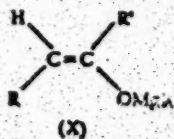
They are able, however, to form both O- and C-derivatives, for example in methoxymethylation (XIII and XIV) [13]:

$$R-CH=C \begin{smallmatrix} R \\ OCH_2OCH_3 \end{smallmatrix} \qquad\qquad \begin{smallmatrix} R-CH-COR' \\ CH_2OCH_3 \end{smallmatrix}$$

(XIII)   (XIV)

the first of which preserves the stereoisomeric relationships.
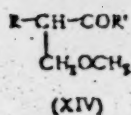
If in the investigations cited there had been no convincing proof of the absence of tautomeric relationships, the results obtained could have been readily explained in terms of the concept of the pseudomerism of metal salts, in the same way as Hückel, for example, has explained the C-alkylation of salts of keto-enol compounds. [14] However, there are no tautomeric relationships here. According to Nesmeyanov, the explanation of the formation of two series of derivatives in absence of tautomerism (in this and other cases) must be sought in the tendency in molecules containing conjugated bonds to undergo "transfer of reaction center" at the moment of reaction under the influence of the attacking reagent and under definite conditions in the reaction medium [15, 16, and 17].

On the basis of these investigations by Nesmeyanov and coworkers, it may be regarded as proved that there are at least two ways in which two series of derivatives (for example, keto and enol) may be formed: first by reversible isomerization with subsequent formation of derivatives from the respective tautomeric forms (keto from the keto forms, and enol from the enol forms); and second by direct formation of keto derivatives from enol forms (or from enolate ions) or enol derivatives from keto forms, which results from reaction proceeding in one elementary act with transfer of reaction center.

Generally speaking, both methods of derivative formation are possible in displaced tautomeric equilibria. It may be shown, however, that in strongly displaced (pseudomeric) tautomeric equilibria, the first method —via preliminary tautomerization —becomes very improbable.

Let us examine a pseudomeric equilibrium between two forms A and B, strongly displaced in the direction of A. Let B react to give B':

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \overset{k_3}{\longrightarrow} B'.$$

There are numerous experimental results showing that tautomeric transformations proceed, formally, as reactions of the first order. As regards the reaction $B \longrightarrow B'$, this may be of a different order. Let us consider a system of two successive reactions, of which the first is of the first order and is reversible, and the second is either of the first or the second order. Let c_0 be the initial concentration (total), a_0 and b_0 the initial concentrations of the forms A and B $[a_0 + b_0 = c_0]$, c, a, b, and b' the corresponding current concentrations: $[a + b = c]$; k_1 and k_2 the rate constants of the forward and back reactions of the tautomeric change, k_3 the rate constant of the unimolecular reaction $B \longrightarrow B'$, k_3' the rate constant of the bimolecular reaction $B + R \longrightarrow B'$; and r_0 and r the initial and current concentrations of the reagent R.

For the equilibrium constant of $A \rightleftharpoons B$, we have:

$$K_T = \frac{b_0}{a_0} = \frac{k_1}{k_2}.$$

We have also the conditions that $k_2 \gg k_1$ and $a_0 \gg b_0$.

A. If the transformation $B \longrightarrow B'$ proceeds much more rapidly than $B \longrightarrow A$, i.e. $k_3 \gg k_2$ or $k_3' r \gg k_2$, the rate of the whole process is limited by the transformation $A \longrightarrow B$. Hence the rate of formation of B' at any given moment will be equal to (or somewhat less than) the rate of formation of B. Equilibrium will then be unable to establish itself, since practically the whole of the substance B formed will be quickly converted into B'. The whole of the conversion of A into B' will then proceed as a reaction of the first order with a constant $q \leqslant k_1$. Since $k_1 = k_2 K_T$, therefore $q \leqslant k_2 K_T$, and hence $q \leqslant k_2 K_T$ (or $q \leqslant k_3' r K_T$).

We can reach the same conclusion on the basis of the full calculation for a system of two successive

reactions of the first order, as carried out by Rakovsky, [18] if we take the fact that $k_2 \gg k_1$ into account[*].

E, If the reaction $B \longrightarrow B'$ proceeds more slowly than $B \longrightarrow A$, then the actual concentration of B will approximate to its equilibrium value (it is equal, or almost equal, to its equilibrium value when k_3 is very small compared to k_2); we may therefore write:

$$b < c \frac{K_T}{1 + K_T} = c \frac{k_1}{k_1 + k_2} = \frac{k_1}{k_1 + k_2} (c_0 - b).$$

The rate of formation of B' when the reaction $B \longrightarrow B'$ is a unimolecular one is therefore:

$$\frac{db'}{dt} < \frac{k_1 k_3}{k_1 + k_2} (c_0 - b)$$

or when it is bimolecular $(B + R \longrightarrow B')$:

$$\frac{db'}{dt} < \frac{k_1 k_3'}{k_1 + k_2} (c_0 - b)(r_0 - b).$$

In either case the process will proceed more slowly than the uni- or bimolecular reaction $A \longrightarrow B'$ would proceed for initial concentration c_0 (and r_0) and rate constants

$$q = \frac{k_1 k_3}{k_1 + k_2} \approx k_3 K_T \text{ or } q' = \frac{k_1 k_3'}{k_1 + k_2} \approx k_3' K_T$$

Whatever the values of the rate constant k_3 or k_3' may be, therefore, the rate of the whole process, proceeding by the pseudomeric mechanism, is limited. The reaction always proceeds more slowly than the direct transformation $A \longrightarrow B'$ with initial concentration c_0 and constants $q = k_3 K_T$ or $q' = k_3' K_T$.

In order to estimate the possible reaction rates of reactions having the pseudomeric mechanism, it is necessary to take into account that for pseudomeric equilibrium the value of K_T is always very small. The constants of many displaced tautomeric equilibria have now been determined: ethyl acetoacetate $(K_{T, H_2O} = 2.2 \cdot 10^{-4})$ [19], ψ-quinolinol $(K_{T, H_2O} = 7.8 \cdot 10^{-5})$ [20], acetone $(K_{T, H_2O} = 2.5 \cdot 10^{-6})$ [21], nitromethane $(K_{T, H_2O} = 4 \cdot 10^{-8})$ [22]. All these, although displaced, are true tautomeric equilibria. By pseudomeric equilibria something different is understood, namely those equilibria in which the concentration of the form B is so low that it is quite impossible to determine the equilibrium constant by modern chemical and physical methods. The constants of pseudomeric equilibria must in any case be not higher than 10^{-10}, and probably of the order of 10^{-12}–10^{-15}. The constant k_2 or k_3 must therefore be 10^{12}–10^{15}

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[*] The differential equations for such reactions $(M_1 \rightleftarrows M_2 \longrightarrow M_3)$ are:

$$\frac{dx_1}{dt} = k_1(a_1 - x_1) - k_2(a_2 + x_1 - x_2).$$

$$\frac{dx_2}{dt} = k_3(a_2 + x_1 - x_2)$$

(Rakovsky's notation), and they give on integration rather complex expressions for c_{M_1}, c_{M_2} and c_{M_3}, which, however, can be considerably simplified when $k_2 \gg k_1$. For the concentration c_{M_3} that is of interest to us (at time t), the exact expression

$$c_{M_3} = a_1 + a_2 + a_3 - \frac{c_1}{q_1} e^{-q_1 t} - \frac{c_2}{q_2} e^{-q_2 t}$$

for $k_2 \gg k_1$, $a_1 \gg a_2$ and $a_3 = 0$, becomes

$$c_{M_3} = a_1 (1 - e^{-q_2 t})$$

in which

$$q_2 = \frac{k_1 + k_2 + k_3}{2} - \frac{1}{2} \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3}.$$

The process therefore proceeds as a first order reaction with an initial concentration of a_1 and a rate constant of q_2.

From the expression for q_2 it will be seen that $q_2 < k_1$ is always true. It follows that $q_2 < k_3 K_T$, and since $k_3 \ll k_2$, we have finally that $q_2 \ll k_3 K_T$.

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times as great as the value of q, the rate constant of the unimolecular reaction, which must proceed more rapidly than the pseudomeric reaction under examination. In the same way, the constant k_3' must be $10^{12}-10^{15}$ times as great as q'.

The reactions to which the concept of pseudomerism is applied are not, however, slow reactions. All of them, on the contrary, are ordinary synthetic organic reactions, proceeding at the moderate speeds that are generally to be observed in laboratories. The numerical values of the unimolecular constants for these reactions lie in the range from $10^{-6}-10^{-4}$ $\sec^{-1}$ to $10-10^2$ $\sec^{-1}$. In this case the constants k_2 and k_3 must have values of the order of greater than 10^6-10^8, and probably than $10^{10}-10^{12}$ $\sec^{-1}$. For the bimolecular constant k_3' values of the order of $10^{10}-10^{11}$ liter $mole^{-1}\sec^{-1}$ and higher must also be assumed.

Rate constants of such an order are not, however, found for organic molecules. Even if such large values may be assumed for k_2 (the process $B \longrightarrow A$, for example, may be the ionization of the enol form and the subsequent recombination of ions to give the keto form), it is impossible to do so for k_3 or k_3'. It is well known that only ions or radicals (or atoms) are able to react with constants of the order of $10^{10}-10^{11}$ liter $mole^{-1}\sec^{-1}$ at moderate temperatures (which correspond to a pseudounimolecular constant of the order of from 10^8-10^9 to $10^{10}-10^{12}\sec^{-1}$, depending on the concentration of the reagent present in excess (from 10^{-2} to 10 moles per $liter^{-1}$). The constants of the reactions of organic molecules are lower by many orders—all the more so for more complex molecules.

We therefore come to the conclusion that, if it is considered that the reaction proceeds by a pseudomeric mechanism, then it is necessary to assume high values for the constant k_3 or k_3' that cannot exist for organic molecules. If, however, we assume that the constant k_3 or k_3' has a possible (i.e. considerably lower) value, then it will be readily seen that pseudomeric reactions ought to proceed exceptionally slowly, which in fact they do not. *

We have carried out the calculation for the limiting case, when the equilibrium constant is of the order of $10^{-13}-10^{-15}$. Experiment, however, shows that also for considerably higher equilibrium constants, of the order of $10^{-2}-10^{-9}$ for example, the reaction does not proceed by the pseudomeric mechanism. We may take as an example the bromination of acetone or nitromethane, which proceeds not via the enol (aci) form, as was at one time thought, but as a result of the direct ionization of the keto (nitro) form.

We do not exclude, of course, the possibility of reaction with intermediate reversible formation of ions or radicals, the concentration of which may be very low, but which are capable of rapid reaction. In this case, however, we are not concerned with the question of pseudomeric equilibrium (of two isomeric organic molecules), but with the equilibrium of dissociation into ions or radicals. There is no question of pseudomerism here.

No place remains, therefore, for the pseudomerism concept. Introduced at the end of last century, when the technique available for the measurement of strongly displaced equilibria was still very poor and the information on the relative rates of chemical reactions was still very meager, it has persisted as an anachronism to the present day, thus greatly interfering with the development of concepts concerning the reactivity of tautomeric substances.

In the treatment of the mechanism of the formation of two series of derivatives by a substance that shows no signs of tautomerism, it is essential to abandon the concept of pseudomeric equilibria displaced to an immeasurably small extent as the cause of dual reactivity. If an equilibrium actually exists and is strongly displaced, for example, toward A, then it may be assumed, with confidence, that the derivative B' is formed not via B, but directly from A without the participation of B.

In the literature various suggestions have been made regarding the possible mechanism of the formation of the derivative B' directly from A without preliminary tautomerization. The old views of Michael [23] were based in such cases on the assumption that a molecule of the reagent (or its elements) adds to A and then splits away again in another order with formation of B'. Huckel criticized this concept [24]. Speculative hypotheses

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*For example, when $K_T = 10^{-12}$ and $k_3 = 1$ ($\sec^{-1}$), $q < 10^{-12}$ ($\sec^{-1}$); when the half period of the reaction is found to be $\tau \geqslant 20,000$ years. Even when $k_3 = 10^4\sec^{-1}$, i.e. for an unusually high rate constant, $\tau \geqslant 2$ years.

of various kinds have been made concerning such reactions on the basis of the "theory of resonance or mesomerism".

In this theory the basis of the explanation of the properties of substances is provided by a false idealistic concept of a multiplicity of molecular structures, each of which is only an imaginary form, but which, when taken together, determine, as a result of "resonance" "superposition", "excitation"), the structure and properties of the molecule. In spite of the fact that these "structures" do not give a representation of the real bonds in the molecule and have a speculative character, material reality has been ascribed to them: they "interact", and to this interaction the meaning of an objectively existing phenomenon "electronic resonance" is given; they "participate" in chemical reactions; they have "weight" and energy of "formation"; they are assigned definite chemical properties; and so on. The real molecule and its actual structure are replaced by fictitious concepts, and A. M. Butlerov's theory of chemical structure is replaced by a perverted theory.

The methodological invalidity and the physical unreasability of the "theory of resonance or mesomerism" were exposed as a result of an extensive discussion in our scientific press and at the Conference on the Theory of Chemical Structure of June 11-14, 1951 [25]. One of the authors of the present paper, Kabachnik, has in the past expounded the "theory of resonance or mesomerism" in an uncritical fashion and has applied it for the explanation of the courses of chemical reactions: in a paper published in "Progress of Chemistry" in 1948 [26], for the explanation of orientation in the benzene ring; and in lectures given as an undergraduate in 1947. His subsequent work over a period of two years on the criticism of the "theory of resonance or mesomerism", in connection with the composition of an article by eight authors in "Progress of Chemistry" [27] and of a report to the Division of Chemical Sciences Committee [28] led the author to an appreciation of the highly erroneous nature of the "theory of resonance or mesomerism", of the completely illusory character of the explanations based on this theory, and of the invalidity of the above-mentioned paper in "Progress of Chemistry" and of the treatment given therein of the phenomenon of orientation in the benzene ring.

The explanations given on the basis of the "theory of resonance" of the formation of two series of derivatives from tautomeric and non-tautomeric substances, are tantamount to the "discovery" of a "resonance structure" responsible for a given series of derivatives. It is clear that such explanations are invalid.

The authors consider that the actual explanation of the formation of two series of derivatives in absence of tautomerism, or under the conditions of very strongly displaced tautomeric equilibria, is to be sought in the concepts developed by Nesmeyanov of conjugation and transfer of reaction center [15]. The field previously assigned to pseudomerism is in actual fact the field of reactions that occur with transfer of reaction center.

III

The concepts developed above are confirmed by the properties of the dialkyl thiophosphites (I and II). They are colorless mobile liquids of characteristic odor. They dissolve in organic solvents and in aqueous alcohol, forming neutral solutions, but they are insoluble in water and in dilute aqueous caustic alkali. They are hydrolyzed by acids and alkalis with quantitative formation of phosphorous acid. They are oxidized by nitric acid, the reaction being very vigorous.

When dialkyl thiophosphites are treated with aqueous-alcoholic alkali, the alkali is gradually consumed, but it is found that the products are not the salts of (II), but sodium alkyl thiophosphites formed by the hydrolysis of one OR group:

(XV)   (XVI)

The consumption of alkali then slows down suddenly and to such an extent that dialkyl thiophosphites may be accurately, though slowly, titrated with alkali. These phenomena are similar to those observed by Nylen [29] for diethyl phosphite. Of the sodium alkyl thiophosphites (phosphorothionates) we have isolated (XV) and (XVI) in the pure state and analyzed them. The acid esters (RO)(HO)PSH, formed by acidification of solutions of these sodium salts with hydrochloric acid, are stable in aqueous solutions and do not alter in them in the course of a month. The solutions that we have found indicate that dialkyl thiophosphites have the phosphorothionate structure (I), and not (II), since the form (II) should have strongly acidic properties. The insolubility of dialkyl thiophosphites in dilute alkalis indicates that if a tautomeric equilibrium (I) ⇌ (II) exists, then it is strongly displaced in the direction of (I) (concerning the hydrolysis of salts of dialkyl thiophosphites, see below).

The conclusion that dialkyl thiophosphites have the structure (I) is confirmed by the results of a determination of the molecular refractions of these compounds [3], as will be seen from Table 1.

TABLE 1

Molecular Refractions of Dialkyl Thiophosphites

Formula	Found MR_D	Calc. MR_D for $(RO)_2 = P \genfrac{}{}{0pt}{}{S\cdot}{H}$	Calc. MR_D for $(RO)_2PSH**$
$(CH_3O)_2PSH$	29.93	29.79	31.91
$(C_2H_5O)_2PSH$	38.91	39.02	41.15
$(C_3H_7O)_2PSH$	48.27	48.26	50.38
$(i-C_3H_7O)_2PSH$	48.64	48.26	50.38
$(C_4H_9O)_2PSH$	57.48	57.50	59.62

* P^V 4.27; $S = 9.70$.
** P^{III} 7.03; $-S-$ 9.06.

Confirmation of the formula (I) can be seen also in the inability that we have found in diethyl thiophosphite to unite with sulfur, cuprous halides, and alkyl halides. Diethyl thiophosphite is readily chlorinated in the cold with evolution of hydrogen chloride and formation of diethyl phosphorochloridothionate:

(I)   (XVII)
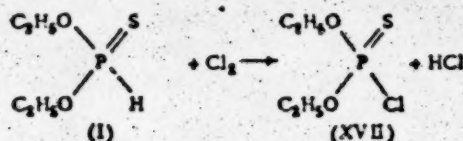
The analysis and constants of the product (XVII), which are identical with those given by the literature [30], leave no doubt concerning its structure.
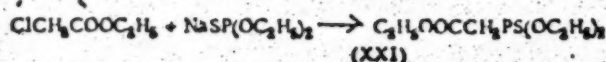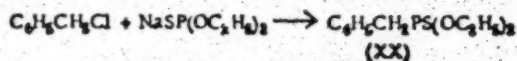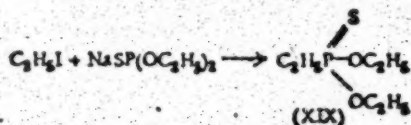
Diethyl thiophosphite, like diethyl phosphite, forms a sodium derivative: by the action of sodium on a benzene solution of diethyl thiophosphite (with evolution of hydrogen) or by the action of sodium ethoxide on diethyl thiophosphite in benzene or alcohol medium.

The sodium derivative of diethyl thiophosphite, unlike free diethyl thiophosphite, vigorously unites with sulfur at room temperature with formation of sodium O,O-diethyl phosphorothiolothionate. This property of the sodium derivative indicates the presence in its molecule of tervalent phosphorus and therefore a structure corresponding to the formula (V). The reaction with sulfur may accordingly be expressed by the equation:
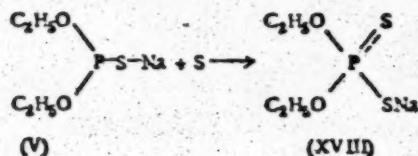

(V)   (XVIII)

From the sodium O,O-diethyl phosphorothiolothionate obtained (XVIII) we have prepared the lead salt $[(C_2H_5O)_2PSS]_2Pb$, m.p. 75-76°. In admixture with authentic lead bis(O,O-diethyl phosphorothiolothionate) it showed no depression of melting point.

The sodium derivative of diethyl thiophosphite reacts in benzene or alcohol medium with alkyl halides, forming the corresponding esters of alkylphosphonothionic acids (i.e. not S- but P derivatives):

(XIX)

$C_6H_5CH_2Cl + NaSP(OC_2H_5)_2 \longrightarrow C_6H_5CH_2PS(OC_2H_5)_2$
(XX)

$ClCH_2COOC_2H_5 + NaSP(OC_2H_5)_2 \longrightarrow C_2H_5OOCCH_2PS(OC_2H_5)_2$
(XXI)

The alkylphosphonothionic esters obtained (XIX and XXI), on being hydrolyzed in sealed tubes with hydrochloric acid, give ethyl chloride and hydrogen sulfide and are converted into the corresponding known phosphonic acids (XXII) and (XXIII) [31,32].

$$C_4H_2P(OH)_2 \qquad\qquad HOOC-CH_2P(OH)_2$$
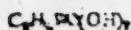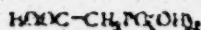
$$(XXII) \qquad\qquad\qquad (XXIII)$$

Diethyl ethylphosphonothionate (XIX), since it contains a $P=S$ bond, should be capable of undergoing Pishchinuka's rearrangement [33]. Actually, when diethyl ethylphosphonothionate (XIX) is heated with ethyl iodide, an isomeric compound, of higher boiling point, specific gravity, and refractive index, is formed. This change in constants is quite characteristic for Pishchinuka's rearrangement:

$$C_2H_5PS(OC_2H_5)_2 \xrightarrow{C_2H_5I} C_2H_5PO(SC_2H_5)(OC_2H_5)$$

$$(XXIV)$$
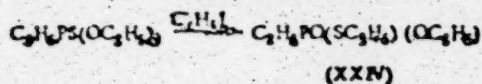
On the basis of the reactions of dialkyl thiophosphites that we have studied, it may be regarded as established that they have the structure (I). Equally, we may consider the structure (V) to be established for the sodium derivative of diethyl phosphite. Finally, there can be no doubt that the products of alkylation with alkyl halides have the structures (XIX-XXI), i.e. are esters of alkylphosphonothionates containing a quinque-valent phosphorus atom. The fact that the free dialkyl thiophosphites have the structure (I) and are insoluble in dilute aqueous alkalis, but in nonaqueous media with alkoxides or sodium form metal derivatives that are readily hydrolyzed by water, undoubtedly indicates the presence of tautomerism (I) ⇌ (II) the equilibrium being strongly displaced in the direction of (I). If the equilibrium did not exist, then the hydrolysis in aqueous solution of the salts of the acid (II), which should be a fairly strong acid (in any case, not weaker than the thiols), would occur only to an insignificant extent. If, on the contrary, there exists an equilibrium between two acids, one of which is a very weak acid, then it is easy to show that the hydrolysis of a salt of such a pair of acids will proceed as if it were the hydrolysis of the salt of the weaker acid.*

The fact that free dialkyl thiophosphites did not enter into addition reactions (with sulfur, for example) we explain by the low effective concentration of the form containing tervalent phosphorus (II) (hence extreme slowness of reaction).

It may be supposed that the formation of a sodium derivative from (I) proceeds with transfer of reaction center:

Transfer of reaction center evidently occurs also in the alkylation with alkyl halides of the sodium derivative of dialkyl thiophosphite, irrespective of whether this reacts as an undissociated molecule:

---

* The hydrolysis constant for the salt of an equilibrium pair of acids (I) and (II):

$$K_{hydr.} = \frac{(c_I + c_{II}) c_{OH}}{c_{A^-}}$$

may be expressed in terms of the ionization constants of the forms K_I and K_{II}:

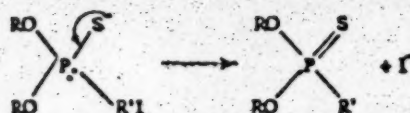$$K_{hydr.} = \frac{K_W (K_I + K_{II})}{K_I K_{II}}$$

(K_W is the ionic product of water). When K_I is very small in comparison with K_{II}, it may be neglected in the numerator, and we obtain:

$$K_{hydr.} = \frac{K_W}{K_I}$$

The hydrolysis of a salt of tautomeric acids proceeds, therefore, as the hydrolysis of a salt of the less acidic form.
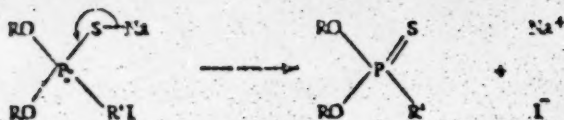
or as the anion:

All the properties found for dialkyl thiophosphites may therefore be explained without the introduction of unfounded concepts of pseudomerism or of resonance (mesomerism).

EXPERIMENTAL

Hydrolysis of Dialkyl "Thiophosphites"

1) A weighed amount of the substance was dissolved in aqueous alcohol (1:1) and slowly titrated with 0.1 N NaOH with phenolphthalein as indicator. The disappearance of the pink color was at first fairly rapid, but became slower and slower, so that toward the end of the titration 5-8 minutes were required for the disappearance of the color due to 2-3 drops of alkali. Diisopropyl thiophosphite was hydrolyzed exceptionally slowly. The results are given in Table 2.

TABLE 2

Equivalent Weight (Hydrolysis of One OR-Group)

Formula	Found	Calculated
$(CH_3O)_2PSH$	127.3; 127.5	125
$(C_2H_5O)_2PSH$	153.0; 153.4	154
$(C_3H_7O)_2PSH$	184.2; 184.0	182
$(C_4H_9O)_2PSH$	210.9; 210.3	210

2) Diethyl thiophosphite (0.9417 g) was dissolved in aqueous alcohol (3:2; 30 ml) and slowly titrated until neutral to phenolphthalein. The volume of 0.1 N NaOH (factor, 1.000) required was 61.08 ml (corresponding to an equivalent weight of 154.2, the calculated value being 154). An immediate addition of 61.08 ml of 0.1 N HCl (factor, 1.000) was made, and it was found that the titer of the solution did not change in the course of one month.

Preparation of Sodium Ethyl Thiophosphite (Phosphonothionate) (XV).

Diethyl thiophosphite (1.54 g) was dissolved in alcohol (3 ml) and water (2 ml), and the solution was mixed with a solution of NaOH (0.40 g in water (3 ml). The alkaline reaction gradually disappeared. The solvent was evaporated over phosphoric oxide in a desiccator, and the salt that remained was washed with ether and dried, yielding very hygroscopic colorless leaves.

Found %: P 20.78; 20.63

$C_2H_6O_2PSNa$. Calculated %: P 20.95

Preparation of Sodium Butyl Thiophosphite (Phosphonothionate) (XVI).

This was prepared in a similar way from 6.3 g of dibutyl thiophosphite and 1.20 g of NaOH. The yield of sodium butyl thiophosphite was 5 g (colorless soft scales).

Found %: P 17.37; 17.12

$C_4H_{10}O_2PSNa$. Calculated %: P 17.61

Action of Sulfur on Diethyl Thiophosphite

A mixture of 15.4 g of diethyl thiophosphite and 3.2 g of sulfur was heated in a water bath for five hours, cooled, and filtered to remove excess of sulfur (3 g). The substance was vacuum-distilled. It had b.p. 64-66°/12 mm and n_D^{20} 1.4586; pure $(C_2H_5O)_2PSH$ has b.p. 67.5-68.5°/12 mm and n_D^{20} 1.4587.

Preparation of Diethyl Phosphorochloridothionate (XVII)

Dry chlorine was passed into diethyl thiophosphite (11.6 g) cooled to −10° until the weight had increased by 5.4 g; hydrogen chloride was evolved. The chlorination product was vacuum-fractionated twice. The fractions obtained at 12 mm were: Fraction I, b.p. 57-81°, 2.8 g; Fraction II, b.p. 81-82°, 6.3 g (45 %). n_D^{20} 1.4711; d_4^{20} 1.1918.

Found %: Cl 18.57; 18.25; S 16.74; 16.53; P 16.40; 16.51

$C_4H_{10}O_2PSCl$. Calculated %: Cl 18.83; S 16.98; P 16.45

For Fletcher and coworkers [36] give b.p. 71.5-72°/7 mm and 95-96°/20 mm, n_D^{28} 1.4685. A preparation obtained by us exactly according to Fletcher's instructions had b.p. 90.5-91.5°/19 mm, $d_4^?$ 1.1899; n_D^{18} 1.4705.

Preparation of Sodium O,O-Diethyl Phosphorothiite (V)

The sodium derivative of diethyl thiophosphite was prepared by the action of finely divided sodium on diethyl thiophosphite in a medium of benzene. There was an abundant liberation of hydrogen, and the sodium derivative separated as a voluminous finely crystalline colorless precipitate. The following method of preparation was found to be preferable: sodium ethoxide was prepared in benzene medium from finely divided sodium and an equivalent amount of alcohol, and the calculated amount of diethyl thiophosphite was then added. Finally, it is possible to add diethyl thiophosphite to an alcoholic solution of sodium ethoxide, but the sodium O,O-diethyl phosphorothiite then remains in solution.

The silver derivative of diethyl thiophosphite was prepared by addition of an equivalent amount of aqueous silver nitrate solution and several drops of ammonia to an alcoholic solution of diethyl thiophosphite; it formed a white precipitate that rapidly darkened in color. It dissolved slowly in benzene with formation of a silver sol.

Reaction of Sodium O,O-Diethyl Phosphorothiite with Sulfur

The sodium derivative was prepared in benzene (12 ml) from diethyl thiophosphite (4.62 g) and sodium (0.69 g). After a short heating and then cooling, flowers of sulfur (0.96 g) were added. The liquid was heated at the boil, and the sulfur dissolved. After one hour the small amount of precipitate was filtered off and the substance was extracted from solution with water. To the aqueous extract a saturated solution of basic lead acetate was added. A colorless lead salt (6.9 g), m.p. 74-75.5°, was obtained. The recrystallized product (6.1 g, from alcohol) melted at 75-76°. In admixture with authentic lead salt [(C$_2$H$_5$O)$_2$PSS]$_2$Pb, it melted at 74.5-75.5°.

Preparation of Esters of Alkylphosphonothionic Acids

Reaction of Sodium O,O-Diethyl Phosphorothiite with Ethyl Iodide. Ethyl iodide (22.8 g) was added slowly to the sodium derivative prepared from diethyl thiophosphite (23.1 g) and sodium (3.44 g) in a benzene medium. The mixture was set aside until it ceased to have an alkaline reaction (four days). The precipitate of sodium iodide was washed out with water, and the benzene solution was dried over sodium sulfate. After three vacuum fractionations, the following fractions were obtained at 13.5 mm: Fraction I, b.p. 72-82°, 2.3 g; Fraction II, b.p. 82-83.5°, 13.7 g (50%); $d_4^?$ 1.0332; n_D^{18} 1.4563.

$$\text{Found \%:} \quad \text{C 39.66; 39.68; H 8.17; 8.13}$$
$$\text{C}_6\text{H}_{15}\text{O}_2\text{SP. Calculated \%:} \quad \text{C 39.56;} \qquad \text{H 8.24}$$

Diethyl ethylphosphonothionate (XIX) is a colorless liquid, soluble in organic solvents and insoluble in water. It is very difficult to hydrolyze; it does not contain P^{III}.

Reaction of Sodium O,O-Diethyl Phosphorothiite with Ethyl Chloride. This was performed as in the preceding experiment. The product from 11.6 g of diethyl thiophosphite, 1.72 g of sodium, and excess of ethyl chloride was 6.1 g (46.5%) of a substance of b.p. 90-93.5°/19 mm; n_D^{18} 1.4545; d_4^{18} 1.0324.

Hydrolysis of Diethyl Ethylphosphonothionate. The substance (XIX) (4 g) was heated with double its volume of hydrochloric acid (1:1) in a sealed tube for three hours at 145-155°. When the tube was opened, the presence of a small pressure of ethyl chloride was revealed. The aqueous solution was evaporated to dryness, and the residue crystallized out when allowed to stand over phosphoric oxide. The crystals were pressed out on a plate and recrystallized from water (by evaporation of the solvent); m.p. 57-58°.

$$\text{Found \%:} \quad \text{P 27.82; 27.82}$$
$$\text{C}_2\text{H}_7\text{PO}_3 \quad \text{Calculated \%:} \qquad \text{P 28.18}$$

For ethylphosphonic acid the literature gives m.p. 60.5-61.5° [31]. Ethylphosphonic acid that we prepared by the reaction of Michaelis and Becker melted at 60°, and a mixture of the two preparations at 58-59°.

Preparation of Diethyl Ethylphosphonothiolate (XXIV). Diethyl ethylphosphonothionate (XIX) (4 g) was heated in a sealed tube with an equal volume of ethyl iodide at 140-150° for three hours. A large amount of (C$_2$H$_5$)$_3$SI crystals were formed in the tube. The liquid was poured from the crystals and was vacuum-fractionated twice, yielding 1.3 g of diethyl ethylphosphonothiolate, b.p. 76-76.5°/4 mm, d_4^{19} 1.0709; n_D^{19} 1.4730.

Found %: C 39.93; 40.08; H 8.25; 7.98; P 17.15; 16.97

$C_8H_{21}O_3SP$. Calculated %:   C 39.56;   H 8.24;   P 17.03

Preparation of Diethyl Benzylphosphonothionate (XX). To sodium O,O-diethyl phosphorothiite prepared in benzene from 7.7 g of diethyl thiophosphite and 1.15 g of sodium, benzyl chloride (6.82 g) was added. Vigorous reaction accompanied by boiling set in. After two days a test of the reaction mixture showed it to be neutral, and the benzene solution was washed with water, dried over sodium sulfate, and vacuum-fractionated. The fraction (5.3 g) of b.p. 124-125°/3.5 mm was separated; it had d_4^{20} 1.1022; n_D^{20} 1.5303.

Found %: P 12.55; 12.62

$C_{11}H_{17}O_2PS$. Calculated %: P 12.70

The substance was a colorless liquid, insoluble in water. After hydrolysis it gave no reaction for P^{III}.

Preparation of Diethyl Ethoxycarbonylmethylphosphonothionate (XXI). Diethyl ethoxycarbonylmethyl-phosphonothionate was prepared in a similar way from 11.6 g of diethyl thiophosphite, 1.72 g of sodium, and 9.2 g of chloroacetic acid. Two distillations yielded 13.0 g (72.2%) of a substance having b.p. 105-106°/5 mm, d_4^{20} 1.1204; n_D^{20} 1.4621.

Found %: C 40.47; 40.43; H 7.05; 6.96, P 12.69; 12.87

$C_8H_{17}O_4PS$. Calculated %:   C 40.00;   H 7.12;   P 12.96

Diethyl ethoxycarbonylmethylphosphonothionate is a colorless liquid, insoluble in water. It is difficult to hydrolyze, and after hydrolysis it gives no reaction for P^{III}.

Hydrolysis of Diethyl Ethoxycarbonylmethylphosphonothionate. The ester (XXI) (2 g) was heated in a sealed tube with HCl (1:1) at 130° for three hours. There was a pressure in the tube when it was opened. The contents were evaporated on a water bath and were evaporated down several times with water in order to remove HCl. The residue crystallized out on standing. The melting point was 138-139°; for carboxymethylphosphonic acid the literature gives 139.5° [34].

SUMMARY

1. The question of pseudomerism has been examined. It has been shown that the concept of pseudomerism demands the assumption of abnormal rates of reaction for organic molecules. The concept of pseudomerism is invalid.

2. It has been suggested that the reactions previously assigned to the field of pseudomerism proceed in fact with transfer of reaction center in the manner indicated by Nesmeyanov, without preliminary tautomeric change.

3. The paper "Orientation in the Benzene Ring", published in "Progress of Chemistry" by one of the authors, Kabachnik, was unsound. The author then adopted the "theory of resonance or mesomerism" in an uncritical fashion, expounded it, and applied it in the explanation of chemical reactions. The author is now thoroughly convinced of the methodological unsoundness and physical invalidity of the "theory of resonance or mesomerism" and regards all explanations of chemical phenomena made on the basis of this "theory" as illusory.

4. The properties of dialkyl thiophosphites have been investigated. It has been shown that the structure of the free dialkyl thiophosphites corresponds to the phosphonothionate formula, in which the phosphorus atom is quinquevalent. The tautomeric equilibrium of dialkyl thiophosphites in solution is very strongly displaced in the direction of the quinquevalent form.

5. It has been shown that dialkyl thiophosphites are able to form metal derivatives containing tervalent phosphorus (phosphorothiites). Alkylation of these yields esters of alkylphosphonothionic acids.

6. It has been suggested that the formation of the sodium derivatives of dialkyl thiophosphites and their alkylation proceed with transfer of reaction center in the manner indicated by Nesmeyanov.

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BRIEF COMMUNICATIONS

RAMAN SPECTRA OF TWO SILAHYDROCARBONS

M. V. Volkenshtein and E. L. Pokrovsky

We have determined the Raman spectra of triethyl (2-methylpropenyl) silane and diallylmethylsilane. As these spectra have not been published previously, we give here the results we have obtained.

Triethyl(2-methylpropenyl)silane $(C_2H_5)_3SiCH C(CH_3)=CH_2$ has b.p. 188.5°/750 mm; n_D^{20} 1.505, d_D^{20} 0.7994. Its spectrum contains the following lines (frequencies in cm^{-1}, visually assessed degree of blackening in parentheses): 142(1), 294(1), 424(1), 490(2), 561(4), 630(1), 964(3), 1013(0), 1042(0), 1107(6), 1127(3), 1173(2), 1228(2), 1297(2), 1371(0), 1409(1), 1459(2), 1630(3), 2783(10), 2880(3), 2910(2), 2956(1), 3081(1), 3130(4).

Frequencies in the range 2783-3130 correspond to valency vibrations of C-H bonds; in range 1371-1459 to deformation vibrations of HCH, 1630 cm^{-1} corresponds to valency vibration of $C=C$, and frequencies in range 900-1100 correspond to valency vibrations of C-C bonds.

Tetramethylsilane has the frequencies: 202(20), 239(15), 598(20), 696(15), 863(10), 1264(10), 1427(15), 2905(10), 2963(10) [1]. Tetraethylsilane has the frequencies 160(4), 249(3), 303(6), 393 (2), 553(10), 625 (3), 736(3), 865(1), 978(5), 1021(5), 1200(7), 1423(7), 1467 (8), 2734(1), 2813(3), 2885(10), 2912(6), 2960(5) [2].

Comparison of the spectra shows that frequencies 142(1) and 294(1) related to deformation vibrations of C-Si-C, and the frequency 561(4) to the valency symmetrical vibration of the group $Si(CH_2-)_3$.

Diallylmethylsilane $CH_3SiH(CH_2CH=CH_2)_2$ has the b.p. 122.5°/745 mm, n_D^{20} 1.4662, d^{20} 0.8055. The spectra contains the following lines: 353(1), 406(3), 556(5), 893(2), 929(1), 983(1), 1116(1), 1153(10), 1190(3), 1234(2), 1296(6), 1392(3), 1493(2), 1627(8), 2117(3), 2801(2), 2900(2), 2972(1), 3097(3), 3083 (2).

The C-H, HCH, C=C, and C-C frequencies lie in the same ranges. The frequency 556(5) corresponds to a valency semisymmetrical vibration of $-Si(CH_2(CH_2-)_3$. The frequency 2117(3) is the valency vibration of the Si-H bond (in SiH_4 2183 cm^{-1}, and in Cl_3SiH 2257 cm^{-1}).

The substances were synthesized by V. F. Mironov in A. D. Petrov's laboratory [3]. We are indebted to A. D. Petrov for providing these substances.

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CHRONICLE

SCIENTIFIC AND TECHNICAL SESSION ON ION EXCHANGE

A Scientific and Technical Session on Ion Exchange was held in Moscow from 3rd to 6th of June, 1952; the meeting was called jointly by the High-parameter Steam Committee of the Energetics Research Institute of the USSR Academy of Sciences, by the Institute of Physical Chemistry of the USSR Academy of Sciences, and by the Institute of Macromolecular Compounds of the USSR Academy of Sciences. Active part in the work of the Session was taken by Institutes of the USSR Academy of Sciences (Institutes of Physical Chemistry and of Macromolecular Compounds, and V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry), the Institute of Organic Chemistry of UkrSSR Academy of Sciences, specialist Institutes (L. Ya. Karpov Institute of Physical Chemistry, All-union Thermotechnical Institute, Institute of Pure Chemical Reagents, Central Institute of the Sugar Industry, All-union Research Institute of the Hydrolysis Industry, Institute of the Nickel and Tin Industry, Leningrad Medical and Pediatric Institute, OTB), and higher education establishments (A. A. Zhdanov Leningrad State University, Kharkov State University, D. I. Mendeleev Moscow Institute of Chemical Technology, Timiryazev Agricultural Academy, Moscow Institute of Chemical Pharmaceutics). Four main questions were discussed at the Session: a) the theory of ion exchange; b) the synthesis of ion-exchange materials; c) the investigation and testing of ion-exchange materials; and d) the application of ion-exchange materials. About forty papers were read at the Session.

In his introductory address the chairman of the organizing committee, Prof. K. B. Chmutov, Doc. Chem. Sci., reported on the implementation of the decisions taken at the conference on chromatography in 1950, gave a brief review of the state of scientific knowledge on the main questions in the program of the Session, and pointed out the most important items, which would require detailed examination. The speaker emphasized that the whole program of the Session was essentially pervaded by chromatography, the method developed by the remarkable Russian scientist M. S. Tsvet and applied in one form or another in all the scientific establishments of the country. Chmutov emphasized also that all the questions to be discussed at the Session represented the further successful development of outstanding work by the Russian scientists K. K. Gedroits, H. A. Shilov, E. N. Gapon, and B. P. Nikolsky. Even a brief exposition of the contents of each of the numerous papers would require much space. We shall therefore examine only the more important results on the fundamental questions discussed at the Session.

a) Theory of Ion Exchange. The following papers were presented in this part of the Session: K. M. Saldadze, Cand. Tech. Sci., (IREA) "Quantitative Laws determining the Ion-exchange Process"; V. V. Rachinsky, Cand. Phys. Math. Sci., (Timiryazev Agric. Acad.) "Present State of Ion-exchange Chromatography"; N. N. Tunitsky, Doc. Chem. Sci. (L. Ya. Karpov Institute) "Theory of the Elution of Chromatographic Bands"; A. T. Davydov, Cand. Chem. Sci., (Kharkov State Univ.) "Laws of Ion Exchange on Soviet-produced Iorites"; M. Ya. Romankevich, Cand. Tech. Sci., (Inst. Org. Chem. Acad. Sci. UkrSSR) "Diffusion Processes in Ion Exchange". The investigations reported at the Session showed that ion exchange on organic ion-exchange materials is a heterogeneous chemical reaction that may be described by the mass action law. At the same time it is necessary to remember that, in addition to the ion-exchange reaction, side reactions, such as hydrolysis, complex formation, reduction, oxidation, etc. may also occur on cationites and anionites. The process of ion exchange under static conditions is most fully described by the equations proposed by B. P. Nikolsky and E. N. Gapon. Prof. O. I. Ryabchikov and M. M. Senyavina, Cand. Chem. Sci., (GEOKhI, Acad. Sci. USSR) criticized work by American authors on the mechanism of ion-exchange chromatography in which complex formers are used, and they reported the results of experimental investigations on the establishment of the nature of the complex compounds and of the relationship between the efficiency of the experiment and the pH of the medium and the concentration of complex-former.

From the discussion of material on the kinetics of ion-exchange processes it was possible to conclude that the kinetics are of a diffusion character. Much interest was aroused by the paper of M. Ya. Romankevich on a new method of measuring diffusion coefficients in an ion-exchange material. In this method diffusion processes are studied in plates of the ion-exchange material. Diffusion coefficients determined by this method are of the same order as those found by the dynamic method (see Prof. N. N. Tunitsky's paper). In

a number of papers material was presented which illustrated qualitatively the direct relation of the swelling propensity of cationites to the kinetic process of ion exchange.

The Session found that in the dynamics of ion exchange there was at present no theory covering the whole complex of questions involved. Two approaches to the solution of this problem were noted. V. V. Rachinsky, Cand. Phys. Math. Sci., (Timiryazev Agric. Acad.) together with T. B. Gapon, Cand. Chem. Sci., (Inst. Phys. Chem.) are working along the lines developed by Prof. E. N. Gapon: the dynamics of ion exchange are treated on the basis of the laws of statics, kinetic factors being considered to play a secondary part. Prof. N. N. Tunitsky and E. L. Cherneva, Cand. Chem. Sci., (L. Ya. Karpov Institute), in developing the dynamics of ion exchange, take the kinetics of the process into account; they treat the dynamics of chromatography in general and do not particularize the theory for the case of ion exchange.

b) Synthesis of Ion-exchange Materials. The magnitude of the contribution in papers to this section bore witness to the hard, fruitful work of Soviet workers on the synthesis of high-quality ion-exchange materials. In particular, papers were read at the session by representatives of the Institute of Macromolecular Compounds of the USSR Academy of Sciences, the State Inst. of Applied Chem., the OTB, the Mendeleev Moscow Inst. of Chem. Tech. Departments of Macromolecular Compounds and of Plastics Technology), and the Frunze Plastics Research Institute. The Session noted that owing to the efforts of a considerable number of organizations the question of the synthesis of home-produced high-quality cationites and anionites must be regarded as solved; nevertheless, commercial production of the brands synthesized by the Institutes is somewhat behind schedule in a number of instances. The Session noted also the need for organizing the sale of ion-exchange materials required for chemical analysis in small packages (in the same way as chemical reagents).

c) Investigation and Testing of Ion-exchange Materials. On this subject the following papers were read at the Session: Prof. D. I. Ryabchikov and M. M. Senyavin, Cand. Chem. Sci., (GEOKhI) "Comparative Study of Certain Ion-exchange Materials"; E. A. Materova, Cand. Chem. Sci., and V. I. Paramonova, Cand. Chem. Sci., (Leningrad State Univ.) "Physicochemical Characteristics of Ionites"; T. B. Gapon, Cand. Chem. Sci., (Inst. Phys. Chem.) "Investigation of the Physicochemical Properties of Ion-exchange Resins with a View to Their Grading and Classification"; Prof. A. A. Vanshteidt, A. A. Vasilyev, Cand. Tech. Sci., and O. I. Okhrimenko, Cand. Tech. Sci., (Inst. Macromol. Comp.) "Titrimetric Method for the Quantitative Determination of Sulfo and Carboxyl groups in Cationites". In these papers the exchange capacity of ionites received the fullest characterization, and in the choice of indexes the speakers based their considerations on the fundamental postulates of the theory of ion exchange. It was shown that it is desirable to determine the total exchange capacity (by the method of potentiometric titration of weighed portions) and the exchange capacity under dynamic conditions. the first index expresses the total exchange capacity under static conditions for all values of the pH of the medium, and the second permits us to estimate the selective action of the sample under investigation and to establish the kinetic properties of the ion-exchange material. Detailed study of a large number of Soviet and foreign ion-exchange materials shows that a number of Soviet cationites and anionites are superior in quality to the best foreign samples. The session gave great attention to the question of a single standard procedure for the testing of ion-exchange materials: one which would permit a sufficiently complete characterization of industrial cationites and anionites by the aid of comparatively few determinations and would enable comparative evaluations of samples to be made. Owing to the great variety of the demands made on ion-exchange materials by different users, the Session recommended all organizations using ionites to let the Chromatography Committee know their specific requirements in order to provide a basis for the coordination of work on the establishment of a single standard method of test.

The question of the investigation of ion-exchange materials was considered by F. G. Prokhorov, Cand. Tech. Chem., All union Thermotechnical Institute, in this paper on "Ionite Materials and the Problem of Chemical Desalting of Natural Waters and Condensates" and by O. N. Grigorov, Cand. Chem. Sci., and L. V. Volf in their paper on "Sulfonated Ion-exchange Adsorbents from Humic Substances". Prokhorov gave some very interesting data on the "aging" of anionites when preserved or used for a long time; as Prokhorov's work shows, "aging" of anionites occurs as a result of their oxidation, which causes amphoteric properties to appear in anionites and leads to an appreciable reduction in exchange capacity.

d) Application of Ion-exchange Materials. A fair number of papers was devoted to this question. We will mention the following: S. M. Chernobrov, Cand. Tech. Sci., (Institute of the P. ... al Industry) "Exchange of Nickel Ions on Cationites"; A. B. Davankov (Lecturer, Moscow Inst. Chem. Tech.) "Extraction of Phenol from Aqueous Solutions by Anionite Resins"; Prof. F. M. Shemyakin (Pharmaceutical Institute) "Use of Soviet Ionite Materials in Chemical Analysis"; Prof. L. T. Solovyev (Leningrad Pediatric Institute) "Separation of Mixtures

of Amino Acids by Ion-exchange Adsorption in Columns of Synthetic Resins"; G. S. Benin, Cand. Tech. Sci., (Sugar Research Institute) "Application of Ionites in the Sugar Industry". M. Ya. Romankevich, Cand. Tech. Sci., (Inst. Org. Chem., UkrSSR Acad. Sci.) "Partial Purification of Sugar Juices by Cationites"; Itenberg, Cand. Tech. Sci. (Novosibirsk Plastics Factory) "Experience Gained in the Use of an Industrial Plant for the Demineralization of Water with Ion-exchange Resins"; B. O. Lyubin, Cand. Tech. Sci., (All-union Research Institute for the Hydrolysis Industry) "Application of Organic Ionites in the Hydrolysis Industry"; a number of papers were devoted to the application of ion exchange materials in fine chemical technology and in the medicinal industry, also to the technical perfection of the chromatographic process. In its resolutions the Session pointed out the need for increasing the range of commercial ion-exchange materials and for reducing their cost, thus widening the field of application of ionites; the Session pointed out also the desirability of developing standard ion-exchange apparatus.

Concrete resolutions were passed on all of the questions considered. These pointed out the direction that must be taken in the further development of the study and application of ion-exchange processes and ion-exchange chromatography. In its general recommendations the Session emphasized the need for setting up a committee on chromatography attached to the USSR Academy of Sciences, for training specialist teams for work on ion exchange and chromatography in the higher education establishments for the study of chemistry, and for the systematic publication of work in journals, collections of articles, and monographs.

The overburdening of the agenda with papers and the absence of sectional meetings reduced the possibility of holding a wide discussion, and this was one of the main faults in the organization of the Session. Note should be taken also of the insufficiently wide notification of workers in institutes and industry of the convening of the session and of the nature of its program.

JOINT SCIENTIFIC SESSION OF THE DIVISION OF CHEMICAL SCIENCES OF THE USSR

ACADEMY OF SCIENCES AND THE ACADEMY OF SCIENCES OF THE UZBEK SSR

On October 24-29, 1952 a Visiting Scientific Session of the Division of Chemical Sciences of the USSR Academy of Sciences was held in Tashkent jointly with the UzbekSSR Academy of Sciences.

The Session assembled in the atmosphere created by the new powerful uplift experienced by the Soviet people, both politically and with respect to production, as a result of the appearance of Comrade Stalin's great work "Economic Problems of Socialism in the USSR" and the resolutions passed by the Nineteenth Congress of the Communist Party of the Soviet Union. The main problems before the Session were the coordination of investigations of workers on chemical questions connected with solution of scientific and economic problems of immediate importance for Uzbekistan and the consideration of the present state and possible further development of these investigations. Considerable attention was devoted to the problem, very important for the national economy of Uzbekistan and of the whole Soviet Union, of the growing of cotton. During the Session, therefore, special conferences were held on the chemistry of mineral fertilizers and on the chemistry and physical chemistry of the cotton fiber.

Considerable importance was attached to personal contacts between scientists, and a beginning was made in this direction in the course of the inspection of the laboratories of the Institute of Chemistry of the Uzbek SSR Academy of Sciences, which was carried out on the the opening day of the Session. Joint discussions began on concrete questions connected with experimental problems facing the chemists of Uzbekistan.

The first meeting of the Joint Scientific Session took place on October 24th in the Sverdlov Concert Hall. Participants in the meetings of the session were members of the Division of Chemical Sciences of the USSR Academy of Sciences, scientific workers of the Institute of Chemistry and other scientific organizations of the UzbekSSR Academy of Sciences, of the Central Asian State University, of the Tashkent Polytechnical Institute, of the UzbekSSR Agricultural Institute, of the Tashkent Textile Institute, and of the Cotton Research Institute, and representatives

of the chemical institutes of the Academy of Sciences of the Uzbek, Armenian and Kazakhan [an Allics and of the various affiliated institutes of the USSR Academy of Sciences, also representatives of industrial undertakings of the Uzbek SSR and teachers from higher educational establishments.

The Session was opened by T. Z. Zakhidov, president of the Uzbek SSR Academy of Sciences. In greeting the participants on behalf of the Presidium of the Uzbekistan Academy of Sciences and the scientists of the Uzbek SSR, T. Z. Zakhidov said that this Session heralded a new stage in the establishment of yet closer scientific and creative cooperation of chemists and representatives of the Uzbekistan chemical industry with other scientists of our great Fatherland.

Iosif Vissarionovich Stalin's great work "Economic Problems of Socialism in the USSR", the historic resolutions of the Nineteenth Congress of the Communist Party of the Soviet Union, and the speech of Comrade Stalin at the Nineteenth Party Congress directed to us Soviet scientists — these form the lodestar in our journey to the solution of the urgent problems of building communism and in the further progress of our advanced Soviet science.

In an exposition of the fundamental problems confronting Uzbekistan chemists T.Z. Zakhidov said that he was sure that the present Session would subject the work of the chemists to critical analysis by means of an extensive exchange of opinions and constructive criticism, that it would consider in a businesslike way the vital problems facing Uzbekistan scientists, and would pave the way for a powerful thrust forward in the study of the chemistry of cotton and in the further development of inorganic, organic, and physical chemistry. T.Z. Zakhidov ended his speech by proposing a toast in honor of the banner-bearer of peace, the eminent man of science, Iosif Vissarionovich Stalin.

Hearty applause greeted the election as Honorary Presidium of the Presidium of the Central Committee of the Communist Party of the Soviet Union, with the great I. V. Stalin, leader of the workers and eminent men of science, at its head.

The chairman at the first meeting, Academician-Secretary of the Division of Chemical Sciences of the USSR Academy of Sciences, M.M.Dubinin, on behalf of the participants in the Session, expressed hearty thanks to the Presidium of the Uzbek SSR Academy of Sciences, to the Bureau of the Division of Technical and Geologo-Chemical Sciences and to the whole community in Uzbekistan for the great amount of work they had put into the organization of the present Session. He expressed his confidence in the success of the work of the Session.

The Joint Session was taking place in a year that had acquired a historic significance in the life of the peoples of the Soviet Union. Two events of enormous importance were associated with this historic year: the appearance of I.V Stalin's great work "Economic Problems of Socialism in the USSR", and the holding of the Nineteenth Congress of the Communist Party of the Soviet Union.

After giving a brief exposition of the work of Honorary Academician I. V. Stalin and of the directives of the CPSS Congress on the growth of production of the most important chemical products, M.M.Dubinin considered the honorable tasks allotted to Soviet scientists in the report rendered by Comrade Malenkov: "to develop further our advanced Soviet science with the object of occupying the first place in world science; to direct the efforts of scientists to the more rapid solution of the problems involved in the utilization of the enormous natural resources our country; and to strengthen the creative cooperation of science with production, remembering that this cooperation enriches science with experience from practice and helps practical workers to solve their problems more rapidly"*, and he expressed his assurance that Soviet chemists would carry out with honor the historic tasks presented to them by the resolutions of the Nineteenth Congress of the Communist Party.

The first paper to be heard was that of I.S.Kanaepolsky, Cand. Chem. Sci. on the subject of "Hydro-technical Cements in the Central Asian Republics". The speaker described investigations on local naturally (gliezh) and artificially (glinites/burnt clays, which were found to be the most suitable additions for the pozzolanization of Portland cement. It has been shown possible to obtain sulfate-stable cements based on Portland cement and gliezh.

The pozzolanic Portland cement having 30% of gliezh which is produced at present in Uzbekistan, although it has a higher water and sulfate-stability than Portland cement, is not as good as sulfate-stable pozzolanic Portland cement prepared with additions of tripolite. The speaker had set himself the task of increasing the sulfate-stability of gliezh Portland cement by changing the mineralogical composition of the cement clinker. Cements have been produced under manufacturing conditions that satisfy the technical requirements for high quality Portland cements. Addition of gliezh greatly increased the sulfate-stability of Portland cement. Pozzolanic Portland cement containing 50% of gliezh, prepared on the basis of cement clinker, was not subject to sulfate aggression. It has been shown

* G. Malenkov, Report rendered to the Nineteenth Congress of the Party on the work of the Central Committee of the All Union Communist Party (Bolsheviks), "Pravda" Press, 1952, p: 62.

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requirements of the constructors of the Main Turkman Canal for use in different zones of the canal.

Local loess-like subsoil clays are of considerable interest for the preparation of hydrotechnical cements; these, on being roasted in the range 650-750°, acquire hydraulic properties. Loess cement hardens better in sulfate solutions than in fresh water. The low stability of loess cement to the atmosphere, which is the result of the deleterious action of atmospheric carbon dioxide, may be eliminated by additions of Portland cement. Loess cement of grade "250" has been approved for hydrotechnical construction and is to be recommended as a high-quality hydrotechnical cement. It has been established that synthetic cements consisting of various proportions of calcium monoaluminate and calcium orthosilicate are very resistant to the agressive action of sulfate- and magnesium-containing waters.

Academicians M. M. Dubinin and S. I. Volfkovich and Corr. Memb. USSR Acad. Sci. V. I Spitsyn took part in the discussion of this paper. They pointed out that hydrotechnical cements were of great importance for the Central Asian Republics, in which one of the greatest works of communism — the construction of the Main Turkman Canal — was being carried out. The utilization of local materials that would improve the quality of the cement was of great practical importance. Hopes were expressed that trials would be made of the effects of additions of surface-active substances at particular stages of the setting and hardening of cement.

Academician S. I. Volfkovich in his paper "Questions of the Chemistry and Technology of Mineral Fertilizers in Central Asia" remarked that the chemization of agriculture presented chemistry, technology, and agrochemistry with immediate problems in the planned study of the optimum conditions for the application of mineral and organic fertilizers under the actual conditions of Central Asia and in the study also of the most suitable means of production, having regard for the raw-material and energy resources and the present-day progress in agrobiology. The speaker cited data on the effectiveness of one ton of nutritive elements in different fertilizers for different types of soils and crops.

The presence of sources of phosphates, sulfur, sulfide ores, potassium and other salts, water power, and fuel in the Central Asian Republics, together with a large demand for fertilizers of high efficiency, makes the problem of the further development here of the manufacture of mineral fertilizers, particularly those providing phosphorous and nitrogen, a very urgent and important one.

It is essential not only to extend the manufacture of superphosphate, but also to study and to bring into use methods of improving the physical properties of superphosphates, increasing the P_2O_5 content, and eliminating the deleterious effect of magnesium compounds on the process. Above all, it is essential to find an effective solution of the difficult problem of enriching phosphorites and to become familiar with processes for the ammoniation of superphosphate and its granulation. By the ammoniation of superphosphate by means of ammoniates it is possible to obtain phosphorous—nitrogen fertilizer containing proportions of nutritive elements close to those required for the main pre-sowing application.

It is possible to obtain another concentrated fertilizer "precipitate" (dicalcium phosphate), containing 32-47% P_2O_5 in a citrate-soluble form. Technically pure dicalcium phosphate is of great interest as a very effective fodder medium for the raising of livestock.

A process that is economical and shows great promise is that for the preparation of "precipitate" with the simultaneous production of calcium or ammonium nitrate by means of a complex process for the decomposition of phosphates with nitric acid. In this process, all the raw material is utilized. In the USSR a number of investigators have developed manufacturing processes for the nitric acid treatment of phosphates not only with the separate preparation of dicalcium phosphate and calcium nitrate, but also with the formation directly of double (nitrogen-phosphorous) or triple (nitrogen-phosphorous-potassium) fertilizers.

Owing to the development of hydroelectic power, the establishment of an electrothermal process for the production of phosphoric acid and its salts (for concentrated fertilizers and feeding media) is of great interest for the future. In the paper, other thermal and thermal alkaline methods for the treatment of phosphates were discussed. Among nitrogenous fertilizers the most satisfactory appeared to be ammonium nitrate. Calcium cyanamide is not only a nitrogenous fertilizer, but also, it has been shown a defoliant for the cotton plant; it has herbicidal

properties. It is possible that the question of its manufacture in the necessary quantities requires further examination. The extension of the manufacture of urea and of its application in agriculture is determined by the economics of production. Potash fertilizers may be suitably applied in Central Asia in the form of concentrated salts: the chloride and sulfate, and in the future, possibly, also the nitrate. It is desirable that part of the fertilizers should be applied as manure mixtures, a suitable component for which is "precipitate" (dicalcium phosphate). The implementation of the directives of the Nineteenth Congress of the Communist Party of the Soviet Union regarding the fertilizer industry in the Fifth Five-Year Plan presents the research organizations with great and urgent theoretical and practical problems.

Academician Volfkovich's paper aroused considerable interest in those present at the Session: he had raised a number of questions. The following took part in the discussion of this paper: M. N. Nabiev, Cand. Tech. Sci. Corr. Memb. Acad. Sci. USSR A.F. Kaputinsky, A.D. Petrov, Academician M.M. Dubinin Active Memb. Acad. Sci. UzbekSSR A.S. Sadykov.

The second meeting of the Joint Session under the Chairmanship of Academician V.M. Rodionov and S. Ya. Yunusov, vice-president of the UzbekSSR Academy of Sciences took place on 25th October at the House of Scientists. The first paper of the meeting was given by Active Memb. UzbekSSR Academy of Sciences. He discussed the results of investigations of the alkaloid-bearing plants of Central Asia and of their alkaloids; these were carried out in the Alkaloid Chemistry Laboratory of the Institute of Chemistry of the UzbekSSR Academy of Sciences. Since the laboratory was established, about 3000 species of plants have been analysed, and a number of very valuable alkaloid-bearing species has been found. The contents and also the quantitative and qualitative changes of the alkaloids in different parts of plants have been studies with respect to their dependence on the conditions of growth and the vegetation periods. It has been found that the green part of alkaloid-bearing plants (stalks and leaves) contains the maximum amount of alkaloids before flowering and fruit-bearing; in the underground parts and the bark the amount of alkaloids becomes less during this time. In dry grass and leaves after the vegetation period there remains a very small amount of alkaloids, and this passes to the underground part and to the seeds, and in the case of woody plants – to the barks.

The reader of the paper and his co-workers have isolated more than 35 new alkaloids: the structures of five of these have been completely proved, for about ten the structures are partially known and the remainder is being studied.

The following took part in the discussion of this paper: Academicians V.M. Rodionov, M.M. Dubinin and S.I. Volfkovich, Corr. Memb. Acad. Sci. USSR B.A. Arbuzov, Prof. G.P. Menshikov, and others; they all expressed high appreciation of these investigations and pointed out the correctness of the line of work – the relating of the search for alkaloids with the growth of the plant — and they pointed out the great theoretical and practical significance of these investigations.

Active Memb. Acad. Sci. UzbekSSR A.S. Sadykov gave a paper on results of investigations on the chemistry of the alkaloids of anabasis. In a discussion of work by A.P. Orekhov and G.P. Menshikov in this field, the speaker reported the results of investigations of the transformation products of anabasine and accompanying alkaloids obtained from anabasis, which were carried out in a laboratory under his direction at the Institute of Chemistry of the UzbekSSR Academy of Sciences. The speaker has succeeded in developing a number of methods that enabled anabasine and lupinine to be prepared in appreciable amount and in adequate purity. The oxidation of anabasine and its derivatives and of a mixture of anabasine and lupinine has been carried out with different oxidizing agents, and the course of the oxidation reaction has been elucidated.

The splitting of anabasine at a C-C bond by the aid of aluminum chloride of sodium is an interesting reaction. A detailed study of this reaction with anabasine and other alkaloids (nicotine, salsolidine) enabled a mechanism to be proposed for the process. Sulfonation of anabasine with pyridine – sulfur trioxide in sulfuric acid under various conditions indicated that the secondary nitrogen as a different character in piperidine than in anabasine. Various sulfonation products of anabasine and its derivatives have been obtained and characterized. The reaction of acrylonitrile with anabasine has also been studied. For the cyanoethylation of anabasine, the effect of water on the rate of the reaction has been determined; the results were explained by the speaker by the partial formation of the ammonium base, which is a catalyst. A wide study has been made of the amination of anabasine and its derivatives. Acetyl derivatives of aminoanabasines have been submitted for pharmacological study.

In addition to the study of the chemistry of anabasine, the alkaloids that accompany anabasine are being investigated. Various derivatives of lupinine have been synthesized. Methods have been developed for the isolation of individual alkaloids from a mixture of the bases. A study is being made of the products of splitting afiline and afillidine with solamide.

The following took part in the discussion of this paper: Academicians V. M. Rodionov and M. M. Dubinin, Corr. Memb. Acad. Sci. USSR N. I. Nikitin, Prof. G. P. Menshikov, and others; they all expressed high appreciation of the investigations on anabasine. Participants in the discussion remarked that the work begun by A. P. Orekhov and G. P. Menshikov had found worthy continuators in the Institute of Chemistry of the Uzbek SSR Academy of Sciences. Much that was of interest from the preparative point of view had been done.

In this paper, Academician V. M. Rodionov gave a review of the present state of the investigation of the chemistry of alkaloids and he gave an account of the immediate problems in this field and in the further study of our alkaloid-bearing flora. A review was given of the discovery of plant bases (morphine, quinine, cinchonine, and cocaine) at the beginning of the nineteenth century and of the study of their properties and structures; the significance of these investigations for the development of theoretical and preparative organic chemistry was discussed. The first attempts at an approach to the syntheses of morphine and quinine led to the synthesis of many important compounds. The study of the properties of quinine and of the accompanying alkaloids from cinchona bark were of no less significance for the development of the chemistry of heterocyclic compounds. The subsidiary alkaloids of opium led to the creation of the chemistry of isoquinoline. The first unsuccessful attempts to synthesize quinine led to the discovery of synthetic dyes and the preparation of remarkable medicinals of the pyrazolone series — antipyrine, pyramidone, analgin and others. Investigations in search of substitutes for morphine were very successful and yielded several preparations of pharmaceutical value (demerol, Soviet promedol, which are superior to morphine in sedative properties, and others). Similar results were obtained also in the investigation of cocaine and other alkaloids.

The main significance of alkaloid chemistry consists in the fact that it leads to a deeper study of heterocyclic compounds and to the syntheses of new substances that are valuable in theoretical, biological and practical respects. Much remains in this field, however, that is unsolved or undeveloped. There is no generally accepted view on the functional role of alkaloids in the life of plants, and the significance of the vegetational period for the formation of alkaloids in plants is not fully established. These investigations, which may have also results of practical value, demand much cooperation between organic chemists and biologists (botanists and physiologists).

Insufficient attention has been given to the thorough study of the active principles of alkaloid bearing plants. In most cases only the alkaloids themselves are studied, to the neglect of the organic acids with which the alkaloids are bound. It is difficult to believe that the acid part is without biological significance. Much more attention must be given to the study of the complexes formed. Apart from these immediate problems, it is very important to elucidate the factors determining the formation of alkaloids in plants and to solve certain other problems closely associated with the physiology of plants. Much work remains to be done also on the further study of our alkaloid bearing flora.

The paper prompted a large number of questions and other contributions; among those taking part were Academician M. M. Dubinin, Active Members Acad. Sci. Uzbek SSR Yu. Yunusov and A. S. Sadykov, Corr. Memb. Acad. Sci. USSR I. N. Nazarov, Corr. Memb. Acad. Sci. Uzbek SSR I. P. Tsukervanik, Prof. G. P. Menshikov.

The third, and final, meeting of the Joint Scientific Session was held under chairmanship of Corr. Memb. Acad. Sci. USSR B. A. Arbuzov and of Active Memb. Acad. Sci. Uzbek SSR A. S. Sadykov on 28th October at the House of Scientists. In opening the final meeting, Academician - Secretary of the Division of Chemical Sciences of the USSR Academy of Sciences M. M. Dubinin gave the sad news of the death of the eminent Soviet Physical chemist Academician Vladimir Aleksandrovich Kistyakovsky. The well known and brilliant investigations of Vladimir Aleksandrovich Kistyakovsky played a great part in their time in the development of Soviet electrochemistry and theory of corrosion. Those present at the meeting paid honor to the memory of V. A. Kistyakovsky by standing.

The first paper was by Cor. Memb. Acad. Sci. UzbekSSR I.P. Tsukervanik on "The Reactions of Acetylene with Aromatic Compounds", in which investigations were described that were based on material relating to the alkylation of the aromatic nucleus with bifunctional compounds.

In reactions with benzene it has been established that addition of FeCl$_3$ and certain other substances to AlCl$_3$ results in an increase in the relative yield of low-boiling fractions, which contain, in this case, styrene (up to 15% of the total yield of products). It has thus been shown that condensation may occur in the direction of the equation $CH \equiv CH + H.A: \longrightarrow A:CH \equiv CH_2$, which is contrary to ideas derived from previous investigations of the impossibility of the formation of aromatic vinyl compounds in this way; ways of creating conditions for the production of higher yields of vinyl compounds can now be indicated.

A detailed study has been made of the condensation of dimethylaniline with acetylene, vinyl chloride, and acetic anhydride in presence of AlCl$_3$ and other catalysts. The conditions have been found for the preparation of di (p-dimethylaminophenyl)ethane in about 40% yield. The nature of anomalous reaction products has been elucidated; they are leuco bases of di- and tri-phenylmethane dyes.

The previously inaccessible and therefore little studied, 1, 1-diarylethanes are of considerable interest as starting materials for various syntheses, some of them can be utilized directly (as components of lubricating oils, antioxidants, etc.) A study has been made of the chlorination, nitration, and sulfonation of diphenylethane and other substances of this series. The chlorination and nitration products are analogs of well known insecticides of the DDT type, their properties are now being studied in detail.

Academicians V.M. Rodionov and M.M. Dubinin, Active Memb. Acad. Sci. UzbekSSR S. Yu. Yunusov, Corr. Members Acad. Sci. USSR I.N. Nazarov, B.A. Arbuzov, A. D. Petrov, and others joined in the discussion.

Corr. Memb. Acad. Sci. USSR I.N. Nazarov in his paper "The Synthesis of Sedatives" gave a short review of the present state of investigations on the synthesis of sedatives and pointed out that until recently the only preparation having a sedative action was morphine, one of the first organic compounds isolated in a pure form (at the beginning of the nineteenth century) and applied in medicine; he described the work carried out under his supervision on the synthesis of new sedatives.

The problem of synthesizing sedatives is largely equivalent to the development of simple and accessible methods for preparing 4-piperidones. An important step forward in investigations on the synthesis of sedatives was provided by investigations carried out under the speakers' supervision, on the devising of new simple methods for preparing heterocyclic compounds, particularly 4-piperidones, from acetylene. The principal reactions in these investigations were condensations of ketones with 1-buten-3-yne. The next stage in the synthesis of sedatives is the introduction, in place of the carbonyl radical of the 4-piperidone, of a phenyl radical and an ether group. The final problem in the synthesis of these compounds is the esterification of 4-phenyl-4-piperidinols to give esters of organic acids. Compounds synthesized by the speaker have been thoroughly investigated with respect to their physiological activity under the supervision of Prof. M. D. Mashkovsky.

These syntheses form an important stage in the development of the chemistry of sedatives, for these compounds when their overall properties are considered, are superior to all other such preparations known at present (morphine lydol, phenadol, etc.) They have a comparatively low toxicity combined with a high sedative activity, about three times as great as that of morphine, without having many of the deleterious properties of the latter (habit forming and other accompanying effects), which is a very important advantage. In promedol medicine has an original Soviet preparation having high activity and a wide field of application. Promedol is not the last word in synthetic organic chemistry. In the near future the appearance of new substances having similar properties may be expected.

— Academicians V.M. Rodionov and M. M. Dubinin, Active Members Acad. Sci. Uzbek SSR A.S. Sadykov and S. Ya. Yunusov, Corr. Memb. Acad. Sci. USSR B. A. Arbuzov, Corr. Memb. Acad. Sci. UzbekSSR I. P. Tsukervanik, and others took part in the discussion on this paper.

Kh. U. Usmanov, Cand. Chem. Sci. in his paper "Recent Physicochemical Investigations of the Cotton Fiber", gave the results of the first systematic investigations of cotton fibers from a large number of selection varieties, obtained in the Natural Polymer Laboratory of the Institute of Chemistry of the UzbekSSR Academy of Sciences and in other

Institutes of the UzbekSSR Academy of Sciences. On the basis of the results obtained and the results of other Investigators of the cotton fiber, the speaker came to the following conclusions:

The fibers of different selection varieties have differing chemical compositions. This difference is found for all the principal substances present in the fiber. The composition depends greatly on the degree of maturity. The degree of polymerization of cellulose varies in different varieties and increases with maturity. This increase is associated with the ripening period of the given variety of cotton plant.

The sorption properties of purified cotton fibers, while varying very little from one variety to another, depend greatly on the degree of maturity. The sorptive capacity of the fiber falls with increasing maturity, the rate of fall being different for different varieties, and being associated also with the ripening periods of these varieties. Sorption and desorption of water by the cotton fiber is slow; this indicates the desirability of constructing cotton driers of the layer type.

The relation between the strength of the fiber and its maturity is different for different varieties. The curve for the dependence of deformation of cotton fibers on their moisture content is of an S-form, and the inflection of the deformation curve for all cellulose fibers corresponds, in general, to the same relative humidity.

The following took part in the discussion of this paper: Academician M. M. Dubinin, Active Memb. Acad. Sci. UzbekSSR A. S. Sadykov and S. Yu. Yunusov, Corr. Members Acad. Sci. USSR N. I. Nikitin and V. A. Kargin, P. I. Zubov, Doc. Sci., V. I. Ivanov, Doc. Sci. Prof. G. D. Vovchenko, Scientific Officers A. S. Sultanov and L. V. Smolina, and others.

The final paper of the third meeting of the Session was given by Corr. Memb. Acad. Sci. USSR V. A. Kargin on the mechanism of the deformation of crystalline polymers.

The speaker pointed out that in the deformation of amorphous polymers all the properties of the material change continuously and the polymer gradually passes from its originally isotropic form into an anisotropic, highly oriented thread. The deformation of crystalline polymers has been regarded in the same way as that of amorphous substances, the difference lying in their content of solid particles—small crystals of the polymer—which play the part of fillers. Investigation of the mechanical properties of such crystalline polymers as polyamides, polyethylene, gutta percha has shown a great difference in the behavior of this group of polymers. At high deformations the change in properties of these polymers proceeds not continuously, but by a jump — a sudden change of the isotropic material directly into a highly oriented thread.

On the basis of an investigation of changes in polymers at high deformations it has been suggested that the deformation of crystalline polymers occurs by means of a phase transformation of the polymer crystals. Those crystals oriented perpendicularly or at a large angle to the direction of the force are broken down, and at the same time new crystals oriented in the direction of the force are formed.

The hypothesis that high deformations of crystalline polymers occur via phase changes in the crystalline part has been directly proved by an X-ray study of isotropic and stretched films of polyethelene. It was found that conversion of the polyethylene to the oriented state is accompanied by formation of a crystalline modification differing somewhat from the crystals in isotropic polyethylene. The very nature of the change in texture during orientation also indicates the disappearance of those crystals that existed in the original isotropic polymer and the appearance of new crystals oriented in the directions of the stretching forces.

The mechanical properties of crystalline polymers are determined by the peculiarities in structure and properties of the crystalline part, which takes an active part in the deformation processes of the material. The difference in mechanical properties between crystalline and amorphous polymers was shown particularly graphically in the case of natural rubber, which can be obtained in both states at one and the same temperature.

Academician M. M. Dubinin, Active Memb. Acad. Sci. UzbekSSR A. S. Sadykov, Doctors of Science N. V. Mikhailov, V. I. Ivanov, K. G. Trofimov, B. G. Zaprometov, and others took part in the discussion of this paper.

The participants of the joint Session agreed with great enthusiasm to send a letter of greetings to I. V. Stalin.

Apart from meetings of the Session, a number of conferences were held on particular questions, with detailed examination of the lines of work of Uzbek scientists.

1. Conference on the Chemistry of Mineral Fertilizers

The conference on the chemistry of mineral fertilizers, which took place in the Institute of Chemistry of the UzbekSSR Academy of Sciences under the chairmanship of Academician S. I. Volfkovich, had two plenary and one laboratory sessions, at which the following papers were heard and discussed:

"Physicochemical Analysis of Processes for the Nitric Acid Treatment of Phosphates" by Academician S. I. Volfkovich; "Some Results of the Work of the Fertilizer Laboratory of the Institute of Chemistry of the UzbekSSR Academy of Sciences" by M. N. Nabiev, Cand. Tech. Sci.; "Phase Distribution of Fluorine Compounds in the Decomposition of Phosphoric Raw Material with Nitric Acid" by Junior Scientific Worker R. A. Ablyazina; "Nitric-acid Decomposition of Kara tau Phosphorites, with Precipitation of Calcium by Sodium Sulfate" by F. M. Mirzaev, teacher in the Faculty of Chemical Technology of the Central Asian Pedagogical Institute; "Agrochemical Requirements in Phosphorus and Nitrogen Fertilizers" by B. P. Machigin, Cand. Agric. Sci.

About sixty people took part in the conference; they included Ministry representatives, and workers from fertilizer factories, from a number of institutes of the UzbekSSR Academy of Sciences, from the Samoilov Scientific Institute of Fertilizers, Insecticides, and Fungicides, and from the Cotton Research Institute of the USSR Ministry of Cotton Growing.

Many of those present took an active part in the extensive discussion that the papers provoked; they included not only chemists and technologists, but also biologists, geologists, and agronomists, and it was possible, therefore, to examine thoroughly all aspects of questions concerning the desirable range of fertilizers that should be available and to coordinate several technological questions with the raw-material resources of Central Asia.

The conference noted that the fulfillment of the directives of the Nineteenth Congress of the Communist Party of the Soviet Union (which contemplated an increase of 88% in mineral fertilizers in 1955, as compared with 1950, and the building of fertilizer factories in excess of immediate requirements in order to ensure the necessary development in production in the succeeding years) must proceed by the improvement and intensification of manufacturing processes, improvement of the physicochemical properties of fertilizers, and the search for better methods of incorporating fertilizers in the soil; it must proceed also by the construction of factories for the production of new kinds of fertilizers. These measures are bound to help not only in the producti_ of the additional amounts of mineral fertilizers required, but also in increasing their agrochemical effectiveness.

The main theme of the work of the Fertilizer Laboratory of the Institute of Chemistry of the UzbekSSR Academy of Sciences is the solution of problems relating to the improvement of the physicochemical properties of nitrogen and phosphorus fertilizers and to the increase of the resources of these fertilizers by the nitric-acid treatment of phosphorite raw material. The results of experiments by the Cotton Research Institute on the desirability of using the siftings obtained in the production of granulated superphosphate for feeding the soil were noted as being of practical value for the technology of fertilizers.

In order to find out more about the agrochemical value of freshly precipitated tricalcium phosphate, as a product of the nitric-acid treatment of phosphates, it is planned to carry out culture and field experiments with phosphates of this kind, both alone and also in admixture with ammonium nitrate, on the saline soils of Central Asia. It was recognized that work must continue on the desirable ratios of active fertilizer components (P_2O_5 and K_2O) in complex and mixed fertilizers and the way they depend on the period of growth of the cotton plant. It was recommended that work should be intensified in the search for new defoliants for the cotton plant which could be prepared from readily available substances that are less toxic for animals than those used at present. As the application of non-root feeding of plants from planes is of such importance, it is desirable to work on the preparation of dry concentrated fertilizers (ammoniated double superphosphate), and also of the corresponding solutions. It was considered that a discussion was desirable, at a separate conference, of the problems and future prospects of the utilization of Central Asian salt resources.

2. Conference on the Chemistry and Physical Chemistry of Cotton

The conference on the chemistry and physical chemistry of cotton, which took place in the House of Scientists under the chairmanship of Corr. Memb. Acad. Sci. USSR V. A. Kargin, had three sessions, at which the following papers were read and discussed:

"Some Present-day Problems in the Theory of the Structure of Cellulose" by V. I. Ivanov, Doc. Tech. Sci.; "Modern Methods for the Chemical Investigation of the Fine Molecular Structure of Cotton Cellulose" by E. D. Kaverzneva, Doc. Chem. Sci.; "Experimental Data on the Physical Chemistry of the Cotton Fiber at Different Periods of Growth" by Kh. U. Usmanov, Cand. Chem. Sci.; "Dependence of the Technological Properties of the Cotton Fiber on the Maturity of the Boll" by M. K. Aleksandrov, Cand. Tech. Sci.; "Main Results and Future Prospects

of Investigations of Selection Varieties of Cotton" by V. V. Laikov, Cand. Tech. Sci.

About seventy scientific workers and specialists in the fields of agrobiochemistry, selection, and the technology of the primary processing of cotton took active part in the work of the conference; they included representatives of the Institute of Chemistry of the UzbekSSR Academy of Sciences, the Institute of Agriculture of the UzbekSSR Academy of Sciences, the Institute of Organic Chemistry of the USSR Academy of Sciences, the Central Research Institute of the Cotton Industry, the Cotton Research Institute, the Central Asian State University, the Institute of Physical Technology of the UzbekSSR Academy of Sciences, the Tashkent Textile Institute, and other scientific institutions and selection stations of Uzbekistan and Tadzhikistan.

In the papers of V. L Ivanov and E. D. Kaverzneva new data were given concerning the chemical heterogeneity of the molecular structure of cellulose, and it was suggested that these phenomena are connected with processes of formation of cellulose in plants and have a bearing on the chemical treatment of the cotton fiber.

In the papers of Kh. U. Usmanov, M. K. Aleksandrov, and V. V. Laikov, new data were given concerning the changes in the structure and chemical and technological properties of the cotton fiber during the growth of the plant, the most interesting being those relating the length, fineness, strength, and sorptive power of the cotton fiber, and the molecular weight of the cellulose it contains, to the degree of maturity of the cotton.

For a number of these very important technical properties of the cotton fiber an optimum has been established in the course of their changes during ripening, and these relations have not yet been fully explained and taken into account in the theory and practice of selection and cultivation of cotton. Moreover, these relations indicate new ways and possibilities, enabling still greater control over the evolution of the cotton plant with the object of increasing still more the efficiency of its production.

In the discussion on these papers, in which chemists, biochemists, technologists, and selection experts took part, the desire was expressed that further, more concrete, application of the data on the chemical heterogeneity of the cellulose molecule should be made to the problems of the chemistry of cotton in the course of growth, with the object of discovering methods for controlling it. Furthermore, attention was drawn to the fact that the time was now ripe for the scientific institutes of Uzbekistan to tackle new problems on the purification of raw cotton, making use of recent advances in cellulose chemistry, and to continue investigations on the controlled oxidation of the substances accompanying cellulose in the cotton fiber, which might lead in the future to the creation of more rational methods of purifying raw cotton and so to an improvement in the treatment of cotton in the textile industry and to the production of cotton goods of improved quality.

There were detailed discussions of many concrete questions of the theory and practice of cotton production related to the mechanism of the appearance and improvement in the course of ripening of technically important chemical and physicomechanical properties of the fiber. At the same time, attention was devoted to long-term research in this field and also to the methods of conducting team investigations directed to the acquiring of more exact information on the laws relating the properties of cotton to the conditions of growth. Emphasis was laid on the need for the development of rapid chemical and physicochemical methods for following the ripening of the cotton fiber throughout its period of growth.

It was noted that this conference was the first general scientific conference of chemists and specialists in the chemistry and physics of cotton cellulose, and it was emphasized that similar conferences were necessary in the future.

3. Conference on Alkaloid Chemistry

The conference on alkaloid chemistry was held in the small conference hall of the Presidium of the UzbekSSR Academy of Sciences under the chairmanship of Academician V. M. Rodionov. There were three sessions, at which 14 original papers were read on alkaloid chemistry:

"Alkaloids of the 1-Methylpyrrolizidine Series" by G. P. Menshikov. Doc. Chem. Sci.; "Alkaloids of Colchicum" by V. V. Kiselev, Cand. Chem. Sci.; "Investigation of Alkaloid-bearing Plants of Central Asia" by E. E. Korotkova, Cand. Bot. Sci.; "Sulfonation of Anabasine" by O. S. Otroshchenko, assistant in the Department of Plant Chemistry of the Central Asian State University; "Cyanethylation of Anabasine" by E. Kh. Timbekova, undergraduate in the Department of Plant Chemistry of the Central Asian State University; "Investigation of the alkaloids of the following: Haplophyllum (junior scientific worker G. B. Sidyakira); Aconitum and Delphinium

(N. N. Abdukhitova, Cand. Chem. Sci.); Aconitum tellassicum (junior scientific worker G. F. Potemkin); Thalictrum minus (N. N. Progeisov, Cand. Chem. Sci.); Vinca erecta (F. Yu. Yuldashev, undergraduate of the Institute of Chemistry); Unicirria Severzowi (Kh. A. Abduazimov, undergraduate of the Institute of Chemistry); Lolium Cuniatum (S. T. Akramov, junior scientific worker); Thermopsis alterniflora (Shch. P. Pakidina, junior scientific worker); Poisonous Weed of the Borage Family (N. V. Plekhanova, undergraduate of the Institute of Chemistry)"; and "Isomerization of Pseudoephedrine into Ephedrine" by D. M. Guseva, junior scientific worker.

About 70 scientific workers of the institutes of the Uzbek SSR Academy of Sciences, the Central Asian State University, and other scientific organizations of Tashkent took part in the work of the conference.

In a series of investigations carried out under the direction of G. P. Menshikov it has been established that the parent substance of all alkaloids of the borage family is the new heterocycle 1-methylpyrrolizidine. A new rational classification of alkaloids of the 1-methylpyrrolizidine series has been proposed. These alkaloids can be divided into four groups: levohellotridan, dextro-hellotridan, levor pseudohellotridan, and dextro pseudohellotridan. It has been shown that, when amino alcohols of the 1-methylpyrrolizidine series are oxidized, isomerization occurs with formation of two stereoisomeric acids. The speaker considered that the role and significance of alkaloids in the life of a plant are directly related to the structures of the alkaloids. Alkaloids of differing structures may play quite different parts in the life of the plant.

From a poisonous weed of the borage family, M. V. Plekhanova has isolated two new alkaloids: incanine and treanidine; they belong to the same 1-methylpyrrolizidine series.

From Colchicum (variety Magnificent) V. V. Kiselev has isolated three alkaloids: colchicine, colchamine, and colchicerine. A proof has been given for the structure of the new alkaloid colchamine, at the basis of which lies the same system as that found in colchicine: colchamine differs from colchicine in having methyl instead of acetyl on the nitrogen, and colchamine is therefore decidedly basic in character. It has been established that colchicerine is a molecular compound of colchicine and colchamine.

E. E. Korotkova gave a general exposition of the results of investigations of the flora of Uzbekistan and neighboring republics with respect to their alkaloid-bearing characteristics. Plants have been investigated at various periods of growth, in various vegetative organs, and in various localities. A list, containing about 2300 plants, of the alkaloid-bearing plants of Central Asia has been drawn up and is being prepared for publication. Weeds found in cereal crops have also been investigated for their alkaloid-bearing characteristics.

O. S. Otroshchenko reported on the sulfonation of anabasine with pyridine—sulfur trioxide and sulfuric acid. In the course of this work, 2,3'–bipyridinesulfonic acid, in which the sulfo group is in the α-substituted pyridine nucleus, has been isolated and characterized. At the same time methods have been worked out for the isolation of anabasine from an anabasine-lupinine mixture and the colorimetric determination of anabasine in the general alkaloid mixture.

E. Kh. Timbekova reported on the reactions of anabasine with acrylonitrile in various solvents. N'–Propylanabasine has been prepared and characterized, and it has been subjected to various reactions, as a result of which about twelve preparations have been sythesized and submitted for pharmacological examination. G. B. Sidyakina has isolated two new alkaloids, haploperine and haplophine, from certain varieties of Haplophyllum, and it has been established that both of these alkaloids belong to the quinoline group; a structural formula has been proposed for haplophine. For one of the varieties a study has been made of the total amount of alkaloids and their approximate proportions at various periods of growth. From three varieties of Delphinium, N. K. Abdakhirova has isolated five new alkaloids and has proved the structures, in part, of three of the alkaloids: delsemine, delsemidine, and delphatine. From one variety of Delphinium, two preparations that can be used as substitutes for curare have been obtained. The preparations are undergoing clinical tests and have been accepted by the State Pharmacopeia Council. Work has begun on the determination of the basic skeleton of the aconite alkaloids. From the aerial part of Aconitum tellassicum, G. F. Potemkin has isolated two known alkaloids, talatisine and talatisamine. The structural formula of talatisamine has been made more precise. Investigations are being carried out with a view to the determination of the structure of the talatisamine nucleus.

From Thalictrum minus N. N. Progeisov has isolated five new alkaloids. It has been established that the alkaloids thalicmine and thalicmidine are aporphine derivatives; the structure of thalicmidine has been proved, and on the basis of a number of regularities to be observed in aporphine alkaloids a structural formula has been proposed for thalicmine. From the aerial part of the plant Vinca erecta F. Yu. Yuldashev has isolated the alkaloid minorine,

and from the roots of the plant three new alkaloids, vincanine, vincanidine, and Base No. 3, have been isolated and characterized. It has been established with the aid of dehydrogenation reactions that vincanine contains an indole and pyridine nucleus. A study has been made of the total and relative contents of the alkaloids at different periods of growth.

Kh. A. Abduazimov has investigated tazetine and two new alkaloids, ungerine and ungeridine, isolated from the plant Ungernia Severzowi. Structural formulas have been proposed for the two new alkaloids. It has been established that ungerine belongs to the phenanthridine series. The position of the methylenedioxy group in ungerine has been demonstrated. In an investigation of the poisonous cerial Lolium cuniatum, S. T. Akramov has isolated and characterized the new alkaloid loline. Preliminary results indicate that this alkaloid is a pyrrolidine derivative.

From the seeds of the plant Termopsis alterniflora, Shch. P. Pakudina has isolated five bases: cytisine, pachycarpine, alternine, alternidine, and Alkaloid No. 5. It was shown that alternine and alternidine are condensation products of cytisine and dichloroethane: alternine is an ethylenedicytisine, and alternidine is a chloroethylcytisine. From cytisine a number of preparations have been synthesized and sent for pharmacological examination. The aerial part of the plant has been studied with respect to the variation in alkaloid content with the period of growth. In the early period of growth, the aerial part of the plant could be used as industrial raw material for the preparation of cytisine.

V. M. Guseva has developed a method for the isomerization of pseudoephedrine hydrogen sulfate to give ephedrine in about 90% yield. A search is now being made for a solvent for the separation of ephedrine after the isomerization, when this is carried out under manufacturing conditions.

All the papers gave rise to lively discussion, which yielded much of value to the participants, who had become quite convinced that work on alkaloid chemistry in Uzbekistan is proceeding very vigorously and giving very valuable results. Those taking part in the discussion emphasized the originality of the line of work followed in the laboratory directed by Active Memb. UzbekSSR Acad. Sci. S. Yu. Yunusov, and they pointed, in particular, to the regularities in the dynamics of the accumulation and formation of alkaloids in plants established by workers of this laboratory. Prof. Menshikov's paper was deserving of special attention: the speaker had given an exposition of his work over many years on the pyrrolizidine alkaloids; he had given a new rational classification of these compounds, and had made some valuable remarks on the part played by alkaloids in plants. V. V. Kiselev's paper had made the question of the structures of colchicerine and colchamine perfectly clear.

The twelve papers by coworkers of Active Members UzbekSSR Acad. Sci. S. Yu. Yunusov and A. S. Sadykov gave a vivid picture of the lines of investigation in the UzbekSSR Academy of Sciences. It should be noted that, in a comparatively short period of time, E. E. Korotkova and her team, working in S. Yu. Yunusov's laboratory, have investigated about 70% of all the plants of Uzbekistan.

4. Conference on Organic Synthesis

The conference on organic synthesis took place in the Faculty of Chemistry of the Central Asian State University under the chairmanship of Corr. Memb. Acad. Sci. USSR A. D. Petrov. About eighty persons took part in the conference, and the following papers were read:

"Hydrogenation of Furfural" by A. S. Sultanova and R. A. Madearikova of the Institute of Chemistry of the UzbekSSR Academy of Sciences, "Petroleum of Lower Uzbekistan" by S. D. Guslakaya of the Organic Chemistry Department of the Central Asian State University; "Cycloalkylation of Aromatic Compounds" by N. G. Sidorova of the same department; "Radical Alkylation of Aromatic Compounds" by E. A. Vdovtsova of the same department; and "Alkylation with Acrylonitrile" by A. V. Grebenyuk of the same department.

There were lively discussions on these papers, in which a number of critical remarks and practical recommendations were made. The practical importance of investigations of furfural was noted. It was noted also that the investigations of I. P. Tsukervanik's school on alkylation were not only of practical, but also of great theoretical interest, since they threw light on the mechanism of the alkylation process and opened up new ways for the synthesis of biphenyl and bicyclohexane hydrocarbons, which were of interest as model hydrocarbons in the investigation of the kerosene fractions of petroleum.

5. Conference on Coal and Petroleum Chemistry

The conference on coal and petroleum chemistry, which took place in the Institute of Chemistry of the Uzbek SSR Academy of Sciences under the chairmanship of Corr. Memb. Acad. Sci. USSR A. D. Petrov, heard papers by the directors of the petroleum and coal laboratories, G. Kh. Kodzhaev, Cand. Chem. Sci., and D. T. Zabramny, Cand. Chem. Sci., relating to the general results of their investigations. Thirty scientific workers of the Institute of Chemistry of the UzbekSSR Academy of Sciences and the Chemistry Department of the Central Asian State University took part in the meeting.

In the discussion of the work of the coal laboratory it was pointed out that serious attention must be given to the important problem of extending resources of coking coals, not only by hydrogenation, but also by other, cheaper methods.

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Apart from the papers given at the main meetings of the Session, and at the specialist conferences, members of the Division, at the invitation of local scientific and public organizations, read a number of papers on questions of interest to scientists and chemists in Tashkent.

On 26 October at the Chemistry Department of the Central Asian State University, a meeting of the Tashkent Section of the D. I. Mendeleev All-Union Chemical Society was held, and papers were read by Corr. Members Acad. Sci. USSR A. D. Petrov and B. A. Arbuzov.

Corr. Memb. Acad. Sci. USSR A. D. Petrov gave a short discussion of the scientific activities of A. M. Butlerov and his students in the Kazan period, and discussed the investigations of Butlerov and his students in the St. Petersburg period in detail. A. D. Petrov devoted special attention to the famous syntheses carried out by the Butlerov school with the aid of organozinc compounds, and he gave a full review of the investigations of A. M. Butlerov's St. Petersburg students and showed in vivid fashion how important their investigations were for the development of organic chemistry.

Corr. Memb. Acad. Sci. USSR B. A. Arbuzov's paper was devoted to a review of the main lines of work of Academician A. E. Arbuzov and his students: a) on the synthesis of organophosphorus compounds; b) on the complex compounds formed by phosphorous esters with certain metal salts; and c) on the application of certain physical methods to the investigation of the structures of organophosphorus compounds.

Corr. Memb. Acad. Sci. USSR A. F. Kapustinsky read a paper at the Central Asian State University entitled "Applications of Physical Chemistry in Geochemistry and Mineralogy," in which he examined, on the basis of a number of examples, the effect of the high pressures existing in the core of the earth on the electron envelopes of the atoms and the conversion of the atoms into the "metallic condition". The basis of the theory of the zonal structure of the earth was explained from the point of view of the theory of atomic structure and thermodynamics, and an exposition was given of the general principles, so important in genetic mineralogy, concerning the sequence of polymorphous changes occurring in crystals as the temperature and pressure rise.

Academician S. I. Volfkovich read a paper in the Polytechnical Institute on the subject of "Crystallization Conditions of Nitrates"; and he read another at the Chirchik Electrochemical Combine on "New Methods for the Manufacture of Nitrogen and Phosphorus Compounds".

Academician A. N. Terenin read a paper in the Central Asian University on "Certain Problems of Photoelectrochemistry".

Prof. G. D. Vovchenko read a paper on "The Palace of our Advanced Soviet Science —the Moscow State University" at the House of Scientists, to a gathering of workers and technologists of the Red Engine Works, and at a meeting of intelligentsia of Samarkand.

At a well-attended meeting for a wide circle of the intelligentsia of Samarkand, held in the Uzbek State University, Academician M. M. Dubinin discussed the enormous problems facing Soviet chemistry and technology, and Academician A. N. Terenin read a paper on photosynthesis. After these papers, members of the Division answered questions from the audience on matters having a direct or indirect bearing on chemistry.

During their visit to Tashkent, members of the Division of Chemical Sciences gave a number of consultations to workers of the Tashkent chemical institutes.

The participants of the Session visited the tomb of Honorary Academician I. A. Kablukov, who died at Tashkent in 1942.

The participants of the Session visited the Stalin Millionaire collective cotton farm and a number of industrial undertakings.

CONCLUSION

The Session was a successful and lively one. All members of the Visiting Session of the Division of Chemical Sciences took an active part in its work. Attention should be drawn to the business-like character of the proceedings and to the interest taken in the work of the Session by scientific workers of Tashkent and other cities of Uzbekistan, and by workers from neighboring republics. The general Session and the specialist conferences went smoothly and had valuable results. A great part of the time was spent in discussion of the papers, and this formed a most valuable part of the work of the meetings. The attendance at the meetings was always high: at the first meeting of the Session more than four hundred were present.

Particular mention must be made of the meeting at Samarkand, in which a wide circle of the intelligentsia of the city took part: more than seven hundred were present.

Moscow and Leningrad chemists made the acquaintance of Uzbekistan chemists and visited the chemical laboratories of the scientific institutes of Tashkent and Samarkand. Scientific contact was effected not only at the meetings of the Session and at the conferences, but also in personal conversations and consultations, etc., which were of great value. This Session has been a great step forward in the establishment of still closer contact between the young chemistry of Uzbekistan and the central research institutes of the USSR Academy of Sciences.

The resolutions passed at the specialist conferences, together with the discussions of the papers read at the meetings of the Session, have created conditions for the attainment of new successes in the development of chemistry in Uzbekistan, and they are contributing to the rise in the creative activity of scientists that is required for the performance of the tasks, stated in the resolutions of the Nineteenth Congress of the Communist Party of the Soviet Union, which are associated with the new powerful uplift that is taking place in the national economy of the country. It must be considered that the main tasks of the Joint Session have been successfully carried out.

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# GEOMETRIC ISOMERISM AND PROPERTIES OF COMPLEX COMPOUNDS

I. I. Chernyaev

From the point of view of a chemist investigating complex compounds and therefore accustomed to working with the concept of the central atom, the difference in properties between ordinary structural isomers follows quite naturally from general chemical ideas concerning the undoubted and necessary dependence of the properties of a substance on its structure. If we take any example of isomerism, say butane-isobutane, then actually, no carbon atom can be found in one isomer that has an inner sphere identical in composition with the inner sphere of a carbon atom of the other.

Let us examine, as an example, the second carbon atom in the butane molecule $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$ and compare the composition of its inner sphere with that of the inner sphere of the second carbon atom in the isobutane molecule

$$\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \end{array} CH\text{-}CH_3$$

It will be seen that in butane the inner sphere is composed of methyl, methylene, and two hydrogen atoms, whereas in isobutane there are three methyls and a hydrogen. Hence, in this case it is quite immaterial what we take as our basis in explaining the difference in the chemical reactions of the isomers: the central atom concept, or the concept of the different distribution of the molecules, each considered as a whole. A distinction in chemical properties is obtained, independently of the way in which we regard the structure of the molecules. Thus, the difference in the chemical behavior of the two isomers is not at all surprising, but appears, on the contrary, to be less than would be expected, for in the whole butane molecule it is impossible to find a carbon atom having an inner sphere of identical composition with that of any of the carbon atoms of the isobutane molecule. This equivalence between the approach from the point of view of the composition of the inner sphere of a central atom and the usual method of organic chemistry—the determination of the degree of chain branching and of the distribution of bonds—is altogether to be expected, for the theory of the structure of complex compounds is in essence a development of the same Butlerov theory of structure. However, with the assumption that the differing behavior of isomers depends only on the composition of the inner sphere, the possibility of explaining this difference in behavior on the basis of the mutual effects of atoms comprising the molecule moves into the background, for it may be found that this difference in the composition of the inner sphere is quite sufficient to explain the differing behavior of isomers.

If we take an analogous example from complex compounds, then it is quite obvious that the following isomers

$$[Pt(NH_3)_4Cl_2][Pt Cl_4] \text{ and } [Pt(NH_3)_3Cl][PtCl_3]$$
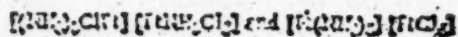
will differ greatly in their chemical behavior, quite independently of the presence or absence of any mutual effects between atoms or being into the inner sphere of the complex. Sufficient cause for their differing behavior is to be found in the fact that the first salt dissociates into singly charged ions, whereas the second gives two doubly charged ions—a difference that is of the same order as that between two carbon compounds exhibiting a double and single bond respectively. On the other hand, the difference in properties may nevertheless depend, in the isomers that we have examined, on the differing spatial arrangement of atoms in the molecule, which in the organic isomers leads to a different degree of chain branching, and in the complex compounds to a differing spatial arrangement of bonds with the central platinum atom.